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RESEARCHES ON THE COMPLEX INORGANIC ACIDS.*

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(Continued from Vol. I, p. 217.)

Phospho-Tungstates.

The phospho-tungstates, as already stated, were discovered by Scheibler, who gave provisional formulas for several different compounds. As the German chemist has published nothing farther upon the subject for six years, and as the study of these compounds seemed to be a necessary preliminary to that of other complex inorganic acids, I have devoted much time and labor to them. The investigation has proved very difficult and tedious, but has yielded results which, if not in all cases perfectly definite and conclusive, are yet as I think valuable and interesting. The difficulties met with in the study of this class of salts are in some respects analogous to those which present themselves in the case of the alkaline tungstates. They are mainly as follows:

1. The normal alkaline phospho-tungstates are readily decomposed by water, yielding acid salts which are often very complex. These acid salts are very slightly soluble, and cannot in general be

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recrystallized for analysis. They are formed in greater or less proportion whenever we attempt to purify the neutral or less acid salts by recrystallization. In many cases the ratio of tungstic and phosphoric oxides in the neutral salt is changed when the acid salt is formed, so that we can draw no certain conclusion from the constitution of one salt as to that of the other. It is usually very difficult, or even impossible, to pass from the acid back to the primitive normal or neutral salt, because the addition of an alkali produces new compounds.

2. It is difficult by any analytical method which has been devised to determine the percentage of phosphoric oxide with great accuracy, and very small differences—often not exceeding 0.2 per cent.—are sometimes sufficient to change the ratio between the number of atoms of phosphoric and tungstic oxides. In the case of tungstic oxide the divisor which we must employ ($WO_3 = 232$) is so large that a very sensible variation in the percentage of the oxide does not sensibly affect the quotient. It is consequently sometimes difficult to decide between formulas in which, for example, the ratios of the two oxides are as 24 : 1, as 22 : 1, or as 20 : 1.

3. For similar reasons it is very difficult to recognize mixtures of different salts.

4. The alkaline phospho-tungstates are usually efflorescent—frequently to a remarkable degree.

5. The salts of the different series agree so closely in physical and chemical properties that, as in the case of the tungstates, distinctive tests are not to be found.

6. It is almost impossible to predict what compound will be formed when tungstates and phosphates or phosphoric acid are mixed, even when the mixture is made with the greatest care and in perfectly definite proportions. Very small variations in the conditions of the process materially affect the results.

7. A large proportion of the salts of this series crystallize only from sirupy solutions, and are consequently difficult to purify by recrystallization.

8. When new salts result from a double decomposition the phospho-tungstate formed does not often correspond in composition to that from which it is derived. It may be of a higher or of a lower order.

Preparation and General Properties.—Scheibler prepared the salts which he has described by boiling neutral or acid sodic tung-

states with half their weight of phosphoric acid. I have found it more convenient to employ the following methods. Solutions of neutral sodic tungstate, $WO_4Na_2 + 2$ aq, and of hydro-disodic phosphate, $PO_4Na_2H + 12$ aq, in the proportion of n molecules of the former to m of the latter, are to be boiled together for some time. The solution has a very strong alkaline reaction. It is to be neutralized with nitric or chlorhydric acid, and then contains the sodium salt—usually acid—of one or another acid of the series. As the sodium salts do not as a rule crystallize as well as those of potassium, I have sometimes found it advantageous to add a solution of potassic bromide or nitrate, when, after some hours, crystals of a potassic salt usually separate in abundance, often in fine colorless and transparent crystals. If a large excess of acid is added at once to the mixed solution of sodic tungstate and phosphate, an acid sodium salt is often precipitated immediately, and almost always after standing a day or two. But it must be remarked that in this case the proportion of tungstic and phosphoric oxides is not always that which existed in the original mixture. In some cases I have fused the tungstate and phosphate together in definite proportions in a large platinum crucible, but this method does not present any special advantage. In other cases I have dissolved tungstic oxide in solutions of alkaline phosphates. Finally, I have in a few instances employed the original method of Scheibler. The alkaline phospho-tungstates, when not too highly acid, are usually rather easily soluble in water, but in the act of solution they almost always undergo a certain amount of decomposition, a white crystalline powder being formed which is comparatively insoluble. Sometimes the solution becomes milky at once, and remains so for a very long time. In all cases it must be allowed to stand until it becomes perfectly clear, and then poured upon the filter without disturbing the precipitate, as the filtrate would otherwise be turbid.

The alkaline phospho-tungstates are not decomposed by hydric sulphide except to a very limited extent. A current of the gas usually produces a blue color from the reduction of a small portion of the tungstic teroxide to the lower oxide W_2O_5. When an alkaline sulphide is added to a solution of a phospho-tungstate a similar reduction is produced. The addition of chlorhydric acid then gives only a small precipitate of tungstic sulphide. Zinc readily reduces a portion of the teroxide to the blue oxide, but the reduc-

tion even after some time is very far from complete. The relations of acid phospho-tungstates to salts of the various alkaloids have already been pointed out by Scheibler. In almost all cases nearly insoluble more or less distinctly crystalline precipitates are formed. I find that a beautiful heavy white crystalline salt is thrown down when an acid phospho-tungstate, as, for example, the sodium salt $24\,WO_3 . P_2O_5 . 2\,Na_2O . 4\,H_2O$, is mixed with a solution of urea, or even with urine. In this last case the precipitate contains also slightly soluble salts of potassium and ammonium. It is possible that the reaction may be utilized in animal chemistry. The phospho-tungstates also precipitate egg-albumen as a white flocky substance, which may prove to be a definite salt, in which case the high molecular weight of the acid would be of great value in determining the equivalent of the compound. I have made no experiments in this direction, and throw out the suggestion for what it may be worth.

Mercurous nitrate precipitates all the phospho-tungstates almost completely. The yellow precipitate formed becomes more dense and compact by boiling with the supernatant liquid. It is nearly insoluble in pure water, but dissolves to some extent even in very dilute nitric acid. Dilute chlorhydric acid decomposes the salt, phospho-tungstic acid being set free. The mercurous salts of the series are the only ones which are sufficiently insoluble to be available in analysis.

Soluble salts of the different series of phospho-tungstates usually possess a strongly marked bitter taste. In a single instance the taste is at once sweet and astringent. The salts which are acid in constitution exhibit a strongly marked acid reaction.

Analytical Methods.—To determine the sum of the percentages of tungstic and phosphoric oxides the salt was dissolved in water or dilute nitric acid, and the two oxides precipitated together by means of mercurous nitrate with the addition of mercuric oxide, as in the estimation of tungstic oxide in the alkaline tungstates already described. This method gives good results only when used with great care, as my assistant, Dr. Gooch, observed that the high temperature and long-continued heat required to expel the whole of the mercury also drove off phosphoric oxide, so that the results frequently varied very materially, and were almost always too low. I have sometimes preferred to precipitate the two oxides with mercurous nitrate in small excess from the boiling solution—as in the case of the

tungstates—and then to evaporate to perfect dryness on a water-bath, continuing the heat until the whole of the free nitric acid was expelled. The dry mass of mercurous phospho-tungstate and basic nitrate adheres somewhat to the evaporating dish, but not so as to render its removal very difficult. Dr. Gooch found that the adhesion was almost entirely prevented by first evaporating the solution and precipitate to a small volume, and then adding water in considerable quantity and evaporating again, this time to perfect dryness. No phosphoric oxide is vaporized on ignition for an hour at a cherry-red heat, and it is not usually necessary to ignite the mixed oxides a second time so as to insure a constant weight, though it is always better to do so. The yellow powder remaining after ignition is a mixture of tungstic oxide, WO_3, and phosphoric oxide, P_2O_5, from which water removes a portion, but not the whole, of the latter. The quantitative determination of the sum of the two oxides by this method is very nearly, but not absolutely accurate. A trace of phosphoric acid almost always remains in the filtrate from the mercurous salt, and may be detected by evaporating this to dryness, expelling the mercurous oxide by heat, and then igniting a portion of the residue with magnesium wire. The loss of phosphoric oxide is, however, extremely small, and probably never exceeds two or three hundredths of one per cent. The tungstic oxide was always determined by subtracting the phosphoric oxide as directly determined from the sum of the two oxides. My various attempts to determine the two oxides together by precipitation with salts of lead or barium, after neutralization with an alkali, proved failures in all cases.

The precise quantitative separation and estimation of phosphoric oxide in the phospho-tungstates is a matter of no small difficulty. After many trials of various methods, the separation by means of magnesia-mixture was found to give the best results, magnesic chloride being employed. Only, in all cases in which this method is used, it is necessary to redissolve the ammonio-magnesic phosphate first precipitated, and to precipitate the salt a second time with ammonia. The whole subject was specially investigated by Dr. F. A. Gooch, and I shall do him and the process the fullest justice by referring to his paper in Volume I of this Journal. Since the publication of Dr. Gooch's paper, I have also used in many cases the following process, which gives excellent results. The phosphoric oxide is to be precipitated in the usual manner as ammonio-

magnesic phosphate, and well washed with magnesia-mixture and ammonia. The precipitate is to be redissolved in chlorhydric acid, ammonia added in small excess, and afterward acetic acid, until the reaction is faintly but distinctly acid. The phosphoric oxide is then to be precipitated from the last solution by uranio-sodic acetate in excess. The precipitate must be allowed to settle completely, and the clear supernatant liquid poured upon the filter without disturbing the precipitate. A moderately strong solution of ammonic nitrate is then to be added, and the precipitate again allowed to settle. After repeating this process two or three times, the precipitate may be brought upon the filter and washed with solution of ammonic nitrate. In this manner there is no danger of obtaining a turbid or milky filtrate. After drying, the precipitate is to be ignited, moistened if necessary with nitric acid, and again ignited. This process is somewhat longer than that by double precipitation and estimation as magnesic pyrophosphate, but is, I think, rather more accurate. In almost all the analyses, by either method, the filtration and washing of the precipitate were effected by means of the asbestos filters devised by Dr. Gooch.* It is hardly possible to speak too highly of this admirable contrivance, which in a very large number of cases is to be preferred to any other mode of filtering, and which has been in daily use in my laboratory for nearly two years, with scarcely a single instance of failure. In many of the earlier analyses the phosphoric oxide was precipitated as ammonio-magnesic phosphate after the addition of citric acid in quantity about equal to the weight of salt taken. Dr. Gooch's later experiments showed that this method gave results which were about 8 per cent. too high when the percipitate—as was always the case—was not redissolved and thrown down a second time. In some cases I have applied this determination as a correction to the direct result of the analysis.

As in the analyses of the alkaline tungstates, I have usually determined the alkali by difference, making direct estimations only in doubtful cases. Ammonia was always expelled by boiling the salt with sodic hydrate, collecting in chlorhydric acid, and weighing as ammonic chloride. Baric oxide was also sometimes estimated by difference. When precipitated from a solution of baric phosphotungstate by sulphuric acid, the sulphate always contains phosphoric oxide, and the same is true when ammonic carbonate and

* This Journal, Vol. I, p. 317.

ammonia are employed. Phospho-tungstates which are insoluble in water may be resolved by fusion with an alkaline carbonate, preferably by the mixed carbonates, CO_3 KNa. Water is best determined from the loss by ignition, but in some cases I have found it best to ignite with a weighed quantity of borax.

Twenty-four-atom Series. Phospho-tungstic Acid.—The acid is most conveniently prepared by decomposing mercurous phospho-tungstate by dilute chlorhydric acid. I have found it best to proceed as follows. To the mixture of 24 molecules of normal sodic tungstate and 2 molecules of sodic phosphate in solution, after boiling for some time, dilute nitric acid free from chlorine is to be added until the reaction is quite distinctly acid. The solution is then to be precipitated hot by mercurous nitrate in small excess, and the yellow flocky mercurous salt washed thoroughly by decantation with hot water. Toward the end of the operation a few drops of solution of mercurous nitrate may be added to the water, as the washings are otherwise apt to become milky. After washing, dilute chlorhydric acid is to be added in small quantities at a time until the yellow color disappears, and is replaced by the white of mercurous chloride. It is well to set aside a small quantity of the mercurous phospho-tungstate, and to add this to the solution of the acid so as to insure the separation of any remaining traces of chlorhydric acid. After complete subsidence the supernatant liquid is to be filtered off clear and then evaporated *in vacuo* over sulphuric acid. The sirupy faintly violet liquid gives splendid large transparent crystals of phospho-tungstic acid, which are sometimes colorless and sometimes sulphur-yellow. The crystals effloresce with great rapidity, and therefore do not admit of measurement. They appear to be regular octahedra. The solution of the acid is colorless, and has a strongly acid reaction and bitter taste. Of these crystals—

1.2791 gr. lost on ignition 0.1809 gr. water		=14.14 per ct.
1.3005 gr. lost on ignition with fused borax 0.1842 gr. water		=14.16 per ct.
1.4151 gr. gave	1.2130 gr. $WO_3+P_2O_5$	=85.72 per ct.
1.5116 gr. gave	1.3201 gr. $WO_3+P_2O_5$	=85.64 per ct.
1.7365 gr. gave	0.0616 gr. $P_2O_7Mg_2$	=2.26 per ct. P_2O_5

The analyses lead to the formula

$$24\ WO_3\,.\,P_2O_5\,.\,6\ H_2O+47\ aq,\ \text{or}\ W_{24}P_2O_{71}(HO)_{12}+47\ aq,$$

which requires :—

		Cal'd.	Mean.		
24 WO_3	5568	83.55	83.57	83.53	83.61
P_2O_5	142	2.13	2.11	2.11	
53 H_2O	954	14.32	14.15	14.14	14.16
	6664	100.00	99.83		

As the phosphoric oxide in the analysis was determined after a single precipitation, a correction of 0.15 is applied to the direct result of the analysis. The crystals had slightly effloresced in drying, which explains the deficiency in the water.

A quantity of the 18-atom potassium salt 18 $WO_3 . P_2O_5 . 6\ K_2O + 26$ aq was dissolved and precipitated by mercurous nitrate. The mercurous salt was then decomposed by dilute chlorhydric acid, and the solution of phospho-tungstic acid obtained evaporated in a flask at about 50° C. by means of a water air-pump, and then allowed to stand in a partial vacuum over sulphuric acid. After some days splendid colorless crystals formed, which appeared to be octahedra, but which on standing became columnar in structure, opaque and yellow. The analyses of these crystals corresponded very closely to the formula

$$24\ WO_3 . P_2O_5 . 6\ H_2O + 34\ aq, \text{ or } W_{24}P_2O_{71}(HO)_{12} + 34\ aq,$$

as the following analyses show:—

1.4482 gr. lost on ignition 0.1636 gr. water = 11.30 per ct.
and gave 0.0492 gr. $P_2O_7Mg_2$ = 2.17 per ct. P_2O_5
1.5109 gr. lost on ignition 0.1708 gr. water = 11.31 per ct.
and gave 0.0521 gr. $P_2O_7Mg_2$ = 2.20 per ct. P_2O_5

		Cal'd.		
24 WO_3	5568	86.59	86.50	86.53
P_2O_5	142	2.20	2.20	2.17
40 H_2O	720	11.21	11.30	11.31
	6430	100.00		

The yellow columnar mass, after re-solution and standing over sulphuric acid *in pleno*, gave perfectly colorless regular octahedra, which corresponded to the formula

$$24\ WO_3 . P_2O_5 . 6\ H_2O + 55\ aq, \text{ or } W_{24}P_2O_{71}(HO)_{12} + 55\ aq.$$

		Cal'd.		
24 WO_3	5568	81.78	81.75	81.76
P_2O_5	142	2.08	2.14	2.15
61 H_2O	1098	16.14	16.11	16.09
	6808	100.00		

In the cases of the two last-mentioned hydrates of the acid, the phosphoric oxide was determined by two successive precipitations as ammonio-magnesic phosphate. The analyses leave no doubt as to the constitution of the acid. Scheibler obtained two different phospho-tungstic acids, to which he gave respectively the provisional formulas

$$H_{15}PW_{11}O_{42}+18\,H_2O, \text{ and } H_{11}PW_{10}O_{38}+8\,H_2O.$$

I should double these and write

$$22\,WO_3 . P_2O_5 . 6\,H_2O+45 \text{ aq, or } W_{22}P_2O_{65}(HO)_{12}+45 \text{ aq.}$$
$$20\,WO_3 . P_2O_5 . 6\,H_2O+21 \text{ aq, or } W_{20}P_2O_{59}(HO)_{12}+21 \text{ aq.}$$

I have not obtained the acid of the 20-atom series, though I shall show further on that there is at least one well-defined salt in which the ratio of tungstic to phosphoric oxide is as 20 to 1. Scheibler does not give the method which he employed for the separation of the two oxides, and I consider it at least probable that his acid

$$22\,WO_3 . P_2O_5 . 6\,H_2O+45 \text{ aq}$$

is identical with the first of the three hydrates which I have described above.

The solution of phospho-tungstic acid forms a colorless heavy oily liquid, with a high refracting power. It has an acid as well as bitter taste, and readily expels carbonic dioxide from carbonates. On standing for some days, the solution undergoes partial decomposition with deposition of a white crystalline powder. This powder is also almost always deposited, in greater or less quantity, in the preparation of the acid, but I could not obtain it in a state of purity sufficient for analysis. It may be worth while to note as a possible source of difference, that Scheibler obtained his acids by the decomposition of the corresponding barium salts by dilute sulphuric acid. The method of preparation which I employed is, I think, preferable.

24 : 2 *Acid Sodic Phospho-tungstate.*—When chlorhydric or nitric acid is added in large excess to a solution of normal sodic tungstate, and of hydro-disodic phosphate containing 24 molecules of the former to 2 of the latter, a salt is obtained which is usually colorless when chlorhydric acid is employed, and pale sulphur yellow when nitric acid is used. This salt crystallizes more easily than the other salts of sodium. According to Dr. Gooch, the small granular crystals appear to be either monoclinic or triclinic. They are readily soluble in water, but invariably undergo a slight decomposition in

the act of solution, a small quantity of a white crystalline powder being formed which is insoluble, or but slightly soluble. The yellow and the colorless crystals have the same crystalline form and the same reactions. Their constitution is also the same, as the following analyses show :—

I.

1.4900 gr. lost on ignition	0.1107 gr. water	= 7.43 per ct.
1.1100 gr. gave	1.0016 gr. $WO_3+P_2O_5$	=90.23 per ct.
1.8072 gr. gave	0.0679 gr. $P_2O_7Mg_2$	= 2.40 per ct. P_2O_5

II.

0.9913 gr. lost on ignition	0.1809 gr. water	= 7.34 per ct.
0.8945 gr. lost on ignition	0.0658 gr. water	= 7.32 per ct.
1.0745 gr. gave	0.9698 gr. $WO_3+P_2O_5$	=90.26 per ct.
1.1508 gr. gave	0.0420 gr. $P_2O_7Mg_2$	= 2.33 per ct. P_2O_5

III.

1.4933 gr. lost on ignition	0.1115 gr. water	= 7.47 per ct.
1.3273 gr. gave	1.1969 gr. $WO_3+P_2O_5$	=90.18 per ct.
1.5424 gr. gave	1.3920 gr. $WO_3+P_2O_5$	=90.25 per ct.
1.2990 gr. gave	0.0470 gr. $P_2O_7Mg_2$	= 2.31 per ct. P_2O_5
1.1503 gr. gave	0.0428 gr. "	= 2.38 per ct. "

IV.

1.8027 gr. lost on ignition	0.1349 gr. water	= 7.48 per ct.
1.1559 gr. lost on ignition	0.0860 gr. water	= 7.44 per ct.
1.1269 gr. gave	1.0151 gr. $WO_3+P_2O_5$	=90.08 per ct.
0.9624 gr. gave	0.0367 gr. $P_2O_7Mg_2$	= 2.44 per ct. P_2O_5
0.6787 gr. gave	0.0263 gr. "	= 2.48 per ct. "

Analyses I and II were made with two different preparations of the colorless crystals; III and IV were made with the sulphur-yellow salt. The determinations of ($WO_3+P_2O_5$) in I, II and III were made by the evaporation process without the use of mercuric oxide, but in IV the oxide was employed. As a check upon the quantity of sodic oxide two direct determinations were made in III, the oxide being weighed as nitrate. In this manner—

1.3273 gr. gave 0.0875 gr. NO_3Na=2.40 per cent.
1.2593 gr. gave 0.0924 gr. " =2.68 per cent. Na_2O.

The mean of these two is 2.54 per cent. As the phosphoric oxide in the analyses above cited was determined from a single precipitation as ammonio-magnesian phosphate, I have, as usual in such cases, applied a correction of 0.15 per cent. to the mean. These analyses lead to the formula

$$24\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O + 23\ aq.$$

or,

$$W_{24}P_2O_{71}(NaO)_4(HO)_8 + 23\ aq.$$

		Calc'd.	Mean.						
24 WO_3	5568	88.10	88.04	87.98	88.08	88.02	88.02		88.09
P_2O_5	142	2.25	2.24	2.25	2.18	2.16	2.13	2.29	2.33
2 Na_2O	124	1.97	2.27	....	....	....	....	....	....
27 H_2O	486	7.68	7.49	7.43	7.32 7.34	7.47	7.50	7.48	7.44
	6320	100.00							

The mean of the five determinations of (WO_3+P_2O_5) is 90.20. The formula requires 90.35. There can, I think, be no reasonable doubt as to the constitution of the acid sodium salt, though it is difficult to obtain it in a state of absolute purity. The salt is very conveniently prepared, however, and makes an excellent reagent for alkaloids. For this special purpose it is best to mix the normal tungstate and hydro-disodic phosphate in the proportion of 24 atoms of the former to 3 or 4 of the latter, boil the mixed solutions for a short time, filter, and add chlorhydric acid in excess, but in small successive portions. A precipitate is usually formed on each addition of acid which disappears on stirring the liquid. On standing, a mass of crystals of the acid salt separates. This should be drained, washed with a little cold water, then dissolved in cold water for a reagent, the clear liquid only being used.

The 24 : 2 acid phospho-tungstate of sodium appears to be always formed when an excess of chlorhydric or nitric acid is added to a solution containing sodic tungstate and phosphate, in which the proportion of the latter to that of the former is as 1 to 12, or as 1 to any number less than 12. In other words, it appears to be the limiting term of all the series. When the salt is fused with sodic carbonate, carbonic dioxide is given off, but not in the proportion which might be expected. In one experiment,

2.2298 gr. lost 0.5408 gr. CO_2 and H_2O = 16.94 per ct.
1.2621 gr. lost on simple ignition 0.0922 gr. H_2O = 7.31 per ct.

The ratio of the WO_3 in the salt to the CO_2 expelled is here as 38 : 22, or very nearly as 24 : 13. If the ratio were as 24 : 13, the reaction would be represented by the equation

$$24\ WO_3 . P_2O_5 . 2\ Na_2O + 13\ CO_3Na_2 = 12\ (2\ WO_3 . Na_2O) + P_2O_5 . 3\ Na_2O.$$

A small proportion of neutral tungstate, WO_4Na_2, is probably formed by the further action of the acid tungstate on the alkaline carbonate.

The 24 : 2 acid sodium salt gives no precipitate with the sulphates of zinc, manganese and copper: a white crystalline precipitate with

argentic nitrate, and after a short time with baric chloride and ammonic nitrate; no precipitates with calcic and strontic chlorides, but after a short time scanty crystalline salts.

The 24 : 2 acid salt is the only sodium compound of the 24-atom series which I have been able to prepare. When a solution of this salt is carefully neutralized with sodic carbonate, the 6-atom or fully saturated salt, $24\ WO_3 . P_2O_5 . 6\ Na_2O$, possibly exists in the solution, but a definite salt could not be obtained by evaporation. When neutral sodic tungstate and hydro-disodic phosphate are mixed in the proportion of 24 : 2, and acetic acid is added to the solution after boiling for some time, no precipitate is formed, but alcohol throws down a colorless oil which soon solidifies to a white gummy mass. I did not obtain a crystalline well-defined salt from this by re-solution and evaporation, but others may perhaps be more successful.

When a sufficient quantity of sodic carbonate is added to a solution of the acid sodic phospho-tungstate, a mixture of sodic tungstate and sodic phosphate appears to be formed.

$$24\ WO_3 . P_2O_5 . 2\ Na_2O + 25\ CO_3Na_2 = 24\ (WO_3 . Na_2O) + P_2O_5 . 3\ Na_2O.$$

The phospho-tungstate is formed again on adding an excess of acid.

24 : 3 *Acid Potassium Salt.*—When a solution of the 24 : 2 acid sodic salt is added to one of a salt of potassium, a heavy white crystalline, very slightly soluble precipitate is formed, either immediately or after a short time. The salt forms very small granular crystals. It requires a large quantity of water for solution, a white, much more insoluble salt being formed in small quantity by the action of water, so that the liquid is, and for a long time remains, milky. It is best, therefore, simply to wash the precipitate with cold water until this begins to give a turbid filtrate, and then to dry the salt by pressure with woolen paper. The salt is also formed when chlorhydric or nitric acid is added to a solution of potassic phosphate and tungstate in the proportion of 2 molecules of the former to 24 molecules of the latter—the two solutions being previously boiled together for some time in a platinum vessel. The reaction in this latter case may be expressed by the equation

$$24\ WO_4K_2 + 2\ PO_4KH_2 + 44\ HCl = 24\ WO_3 . P_2O_5 . 3\ K_2O + 44\ KCl + 24\ aq,$$

and in the case of precipitation by the acid sodium salt, by the equation

$$24\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O + 6\ KNO_3 = 24\ WO_3 . P_2O_5 . 3\ K_2O . 3\ H_2O + 4\ NaNO_3 + 2\ NO_2H + 3\ H_2O.$$

In this salt—

1.1478 gr. gave	1.0588 gr. $WO_3 + P_2O_5$	= 92.25 per ct.
1.1764 gr. "	0.0468 gr. $P_2O_7Mg_2$	= 2.54 per ct. P_2O_5
1.7383 gr. lost on ignition	0.0576 gr. water	= 3.31 per ct.
1.7638 gr. " "	0.0578 gr. "	= 3.28 per ct.

The analyses lead to the formula

$$24\ WO_3 . P_2O_5 . 3\ K_2O . 3\ H_2O + 8\ aq.$$

		Calc'd.	Mean.		
24 WO_3	5568	89.93	89.86	89.86	
P_2O_5	142	2.29	2.39	2.39 corrected.	
3 K_2O	283	4.57	4.45	....	
11 H_2O	198	3.19	3.30	3.28	3.31
	6191	100.00	100.00		

In another preparation of the same salt,

0.7340 gr. gave	0.6660 gr. $WO_3 + P_2O_5$	= 90.74 per ct.
1.1400 gr. "	1.0317 gr. "	= 90.50 per ct.
0.8028 gr. "	0.0310 gr. $P_2O_7Mg_2$	= 2.47 per ct. P_2O_5
1.5568 gr. lost on ignition	0.0805 gr. water	= 5.17 per ct.
0.8822 gr. " "	0.0455 gr. "	= 5.16 per ct.

The analyses correspond to the formula

$$24\ WO_3 . P_2O_5 . 3\ K_2O . 3\ H_2O + 14\ aq.$$

		Calc'd.	Mean.		
24 WO_3	5568	88.38	88.30	88.42	88.18
P_2O_5	142	2.26	2.32	2.32	
3 K_2O	283	4.49	4.21	. . .	. . .
17 H_2O	306	4.87	5.17	5.16	5.17
	6299	100.00	100.00		

24 : 3 *Acid Ammonium Salt.*—When a solution of a salt of ammonium is mixed with one of sodic tungstate and phosphate, no precipitate is formed, even after standing; but if a large excess of chlorhydric or nitric acid is poured in, a white or very pale yellowish heavy crystalline salt is thrown down in large quantity. This salt is an acid phospho-tungstate of ammonia, the constitution of which varies with the proportions of the salts employed in its preparation and with the conditions of the experiment.

The different salts, however, resemble each other very closely, and may be described in the same terms. They are either perfectly white or have in mass a faint tinge of yellow and an extremely fine-grained crystalline structure. They are very slightly soluble even

in hot water, and give milky emulsions which settle very slowly. Like many other phospho-tungstates and tungstates, they are difficult to wash, as they pass through the closest filter-paper with extraordinary facility. This difficulty may, however, be overcome by adding ammonic nitrate to the wash-water. The acid phospho-tungstates of ammonium are soluble in ammonia-water, but the crystals obtained from such solutions are either ammonic tungstates or salts of series different from that to which the salt dissolved belonged. They are readily decomposed by a red heat, leaving a mixture of tungstic and phosphoric oxides. When boiled with mercurous nitrate, they yield mercurous salts and ammonic nitrate.

In one preparation in which sodic tungstate and phosphate were mixed in the proportion of 20 atoms of the former to 2 of the latter, ammonic nitrate was added, and afterward nitric acid. The precipitate was washed with solution of ammonic nitrate, and afterward with alcohol and water, and dried by pressure with woolen paper. Of this salt,

1.3460 gr. lost on ignition 0.1405 gr. $H_2O+NH_3=10.44$ per ct.
1.6407 gr. lost on ignition 0.1707 gr. $H_2O+NH_3=10.40$ per ct.
1.2038 gr. gave 0.0430 gr. $P_2O_7Mg_2=2.27$ per ct. P_2O_5 (twice precip.)
1.3960 gr. gave 0.0504 gr. $P_2O_7Mg_2=2.31$ per ct. " "
1.4890 gr. gave 0.0720 gr. NH_4Cl $=2.35$ per ct. $(NH_4)_2O$.

These analyses lead to the formula

$$24\ WO_3 . P_2O_5 . 3\ (NH_4)_2O . 3\ H_2O + 26\ aq.$$

		Cal'd.	Mean.		
24 WO_3	5568	87.17	87.29	87.27	87.31
P_2O_5	142	2.22	2.29	2.27	2.31
3 $(NH_4)_2O$	156	2.44	2.35	2.35	
29 H_2O	522	8.17	8.07	8.05	8.09
	6388	100.00	100.00		

It will be observed that in this case the 24-atom salt was obtained under conditions which *a priori* should have yielded a 20-atom salt. I have already stated that salts of urea are precipitated from their solutions by acid sodic phospho-tungstate $24\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O$. The precipitation is, however, not complete, and the process does not appear to be available as a method of analysis.

When phosphate of aniline and 10 : 4 sodic tungstate are dissolved together, and the solution is boiled for a short time, chlorhydric acid gives an abundant yellowish-white precipitate. On re-solution the precipitate yields pale sulphur-yellow crystals, which

are readily soluble in alcohol. Phosphate of para-toluidine behaves in a similar manner; the phospho-tungstate formed is readily soluble, and crystallizes in long yellow silky needles.

I did not succeed in making the insolubility of the acid ammonic phospho-tungstate available in analysis, either for the determination of ammonia or for that of phosphoric acid. For the last-named estimation the phospho-molybdates appear to be far better adapted.

24 : 3 *Acid Barium Salt.*—When 10 : 4 sodic tungstate is dissolved and a small quantity of phosphoric acid is added, the hot solution gives with baric chloride a heavy white flocky precipitate, which readily dissolves in hot dilute chlorhydric acid. The solution, after filtration from a small quantity of flocky matter, is pale yellow, and after some time deposits splendid nearly colorless crystals, which appear to be octahedra. These are readily soluble in hot water without decomposition, and may be repeatedly crystallized without difficulty. Of these crystals,

0.7672 gr. gave	0.6278 gr. $WO_3+P_2O_5$	=81.83 per ct.
1.5557 gr. lost on ignition	0.1872 gr. water	=12.03 per ct.
1.3732 gr. lost on ignition	0.1641 gr. water	=11.95 per ct.
1.6196 gr. gave	0.1547 gr. SO_4Ba	= 6.27 per ct. BaO
and	0.0581 gr. $P_2O_7Mg_2$	= 2.29 per ct. P_2O_5
1.2694 gr. gave	0.1158 gr SO_4Ba	= 6.28 per ct. BaO

The analyses agree fairly well with the formula

$$24\ WO_3\ .\ P_2O_5\ .\ 3\ BaO\ .\ 3\ H_2O+43\ aq.$$

or,

$$W_{24}P_2O_{71}(BaO_2)_3(HO)_6+43\ aq.$$

The same salt is formed when two atoms of 12 : 5 sodic tungstate are boiled for a time with two atoms of sodic phosphate and chlorhydric acid is added in excess. Baric chloride then gives after a time crystals exactly similar to those described above. In a salt prepared in this manner,

1.0020 gr. gave	0.8173 gr. $WO_3+P_2O_5$	=81.56 per ct.
1.4718 gr. gave	0.1648 gr. SO_4Ba	= 6.97 per ct. BaO
and	0.0518 gr. $P_2O_7Mg_2$	= 2.25 per ct. P_2O_5
1.4841 gr. lost on ignition	0.1717 gr. water	=11.57 per ct.

		Calc'd.	Mean.			
24 WO_3	5568	79.57	79.57	79.69		79.46
P_2O_5	142	2.03	2.12	2.14		2.10
3 BaO	459	6.56	6.62	6.27	6.28	6.97
46 H_2O	828	11.84	11.78	12.03	11.95	11.57
	6977	100.00	100.09			

The phosphoric oxide determinations are corrected in both analyses. The percentage of baric oxide as determined by difference, which is the more accurate method, is 6.53. The salt effloresces with extraordinary rapidity, so that it is very difficult to dry it for analysis by pressure between folds of woolen paper.

Twenty-two-atom Series.—The phospho-tungstates containing 22 atoms of tungstic oxide to 1 of phosphoric oxide are represented by apparently well-defined salts of potassium, sodium and ammonium. I have not succeeded in preparing the corresponding acid. As already stated, Scheibler has given provisionally the formula

$$H_{15}PW_{11}O_{43}+18\ H_2O, \text{ or } 22\ WO_3 . P_2O_5 . 6\ H_2O+45\ aq,$$

to an acid which he obtained by the decomposition of a salt of barium, and it may be that this is really the acid of the 22-atom series. Further investigations must decide the point. The salts of the 22-atom series closely resemble those of the 24-atom series already described, and are only to be distinguished from them by analysis.

22 : 2 *Potassium Salt.*—The 18-atom potassium salt,

$$18\ WO_3 . P_2O_5 . 6\ K_2O + 30\ aq,$$

gives with chlorhydric or nitric acid a heavy white fine granular precipitate of an acid salt which belongs to the 22-atom series, and which has the formula

$$22\ WO_3 . P_2O_5 . 2\ K_2O . 4\ H_2O + 2\ aq,$$

as the following analyses show:

1.5679 gr. lost on ignition 0.0318 gr. water = 2.03 per ct.
1.0728 gr. lost on ignition 0.0222 gr. water = 2.07 per ct.
1.5061 gr. gave 1.4250 gr. $WO_3 + P_2O_5$ = 94.61 per ct.
1.1873 gr. gave 1.1253 gr. $WO_3 + P_2O_5$ = 94.78 per ct.
2.1607 gr. gave 0.0927 gr. $P_2O_7Mg_2$ = 2.74 per ct. P_2O_5
2.2367 gr. gave 0.0950 gr. $P_2O_7Mg_2$ = 2.72 per ct. "

		Calc'd.	Mean.		
27 WO_3	5104	92.08	92.11	92.20	92.03
P_2O_5	142	2.56	2.58	2.59	2.57 corrected.
2 K_2O	189	3.41	3.26	....	....
6 H_2O	108	1.95	2.05	2.03	2.07
	5543	100.00			

The salt is very slightly soluble in water. The solution becomes milky, and remains so for a long time. Its formation from the normal 18-atom salt may perhaps be expressed by the equation,

$$10\ (18\ WO_3 . P_2O_5 . 6\ K_2O) + 84\ HCl + 36\ H_2O = 9\ (22\ WO_3 . P_2O_5 . 2\ K_2O . 4\ H_2O) + 2\ (P_2O_5 . 3\ K_2O) + 84\ KCl + 42\ H_2O.$$

22 : 3 *Ammonium Salt.*—An acid ammonium salt of this series was obtained from a mixture of sodic tungstate and phosphate, to which ammonic nitrate and excess of chlorhydric acid had been added exactly as in the preparation of the 24-atom salt already described. The salt was in very small colorless granular crystals, slightly soluble in cold water, but dissolving to some extent in hot water, giving a milky liquid, settling very slowly. Its other properties are not distinguishable from those of the 24-atom salt. Of this salt,

Gr.		Gr.		Per ct.	Per ct.	
0.8697	lost on ignition	0.0805	water and ammonia	= 9.26	= 90.73	$WO_3 + P_2O_5$
1.5911		0.1470		= 9.24	= 90.76	"
0.9086		0.0837		= 9.21	= 90.79	"
1.0934		0.1009		= 9.21	= 90.79	"
1.0934 gave		0.0439	$P_2O_7Mg_2$	= 2.63	P_2O_5	
1.7970 gave		0.0993	NH_4Cl	= 2.68	$(NH_4)_2O$	

These analyses correspond very closely to the formula,

$$22\ WO_3 . P_2O_5 . 3\ (NH_4)_2O . 3\ H_2O + 18\ aq,$$

which requires:

		Calc'd.	Mean.				
22 WO_3	5104	88.30	88.29	88.25	88.28	88.31	88.31
P_2O_5	142	2.46	2.48	2.48 corr.	....	....	....
3 $(NH_4)_2O$	156	2.69	2.68	2.68	...	....	....
21 H_2O	378	6.55	6.60	6.58	6.56	6.53	6.53
	5780	100.00	100.05				

22 : 2 *Sodium Salt.*—It has already been mentioned that, in the preparation of the acid sodium salt of the 24-atom series, a white very slightly soluble crystalline powder is formed in greater or less quantity. This salt cannot be recrystallized for analysis, and must therefore be washed with cold water to remove traces of the soluble acid salt. Hot water dissolves it in small proportion only, the solution remaining milky for a long time. In one preparation of this salt,

0.8405 gr. gave 0.7962 gr. $WO_3 + P_2O_5$ = 94.73 per cent.
0.8405 gr. gave 0.0330 gr. $P_2O_7Mg_2$ = 2.51 per ct. (twice precip.) P_2O_5
1.4990 gr. lost on ignition 0.0403 gr. water = 2.69 per ct.

These analyses lead to the formula

$$22\ WO_3 . P_2O_5 . 2\ Na_2O . 4\ H_2O + 5\ aq.$$

		Calc'd.	
22 WO_3	5104	92.26	92.28
P_2O_5	142	2.56	2.51
2 Na_2O	124	2.25	2.58
9 H_2O	162	2.93	2.69
	5532	100.00	

22 : 4 *Barium Salt.*—This salt was obtained by mixing neutral sodic tungstate and hydro-disodic phosphate in the proportion of 24 : 2, neutralizing with acetic acid, and adding a solution of baric chloride. Small sharp prismatic crystals formed after a short time, soluble in hot water apparently without any decomposition, and separating again from the solution in colorless needles. Of this salt,

0.6900 gr. gave 0.5494 gr. $WO_3+P_2O_5$ = 79.62 per ct.
0.6900 gr. gave 0.0826 gr. $P_2O_{11}U_2$ = 2.34 per ct. P_2O_5
0.6734 gr. gave 0.5372 gr. $WO_3+P_2O_5$ = 79.71 per ct.
1.5296 gr. gave 0.2163 gr. SO_4Ba = 9.24 per ct. BaO
0.9682 gr. lost on ignition 0.1076 gr. water = 11.12 per ct.
0.7064 gr. lost on ignition 0.0787 gr. water = 11.14 per ct.

These analyses lead to the formula

$$22\ WO_3 . P_2O_5 . 4\ BaO . 2\ H_2O + 39\ aq.$$

or,

$$W_{22}P_2O_{65}(BaO_2)_4(HO)_4 + 39\ aq.$$

		Calc'd.	Mean.		
22 WO_3	5104	77.37	77.33	77.37	77.28
P_2O_5	142	2.15	2.34	2.34	
4 BaO	612	9.28	9.24	9.24	
41 H_2O	738	11.19	11.13	11.12	11.14
	6596	100.00	100.04		

The phosphoric oxide was precipitated twice.

(To be continued.)

CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE COLLEGE.

No. VI.

ON THE DETECTION AND DETERMINATION OF ARSENIC IN ORGANIC MATTER.

By R. H. Chittenden and H. H. Donaldson.

There have been many different methods devised for the detection and determination of arsenic in organic matter, but few are entirely free from objectionable features, or sufficiently accurate to insure perfect reliance upon results obtained by their use. At the present day the toxicologist is expected to answer questions as to rapidity of absorption and rate of elimination, and is required to follow the track of the poison step by step in its course through the body. He has need of methods which will allow of its detection with certainty even though present in very minute quantity. And when by chemical evidence alone the toxicologist is required to state whether the poison has been introduced into the body long before death, or, in other words, whether it is a case of acute or chronic poisoning, none but the most accurate method will suffice to give the information needed. Recently Gautier,* recognizing the need for physiological purposes of a more trustworthy method for the determination of arsenic in animal tissue, has described a new process which has in it many commendable features, but which requires reagents certainly not always obtainable in a state of purity or free from arsenic, though a smaller number is needed than in the commonly used method of Fresenius and Babo.

That a method which requires ten or twelve different chemicals for its completion in the detection of arsenic is a dangerous one, especially in medico-legal cases, no conscientious worker can deny; and a method which involves the use of hydrogen sulphide for 12 to 24 hours will no doubt be gladly dispensed with by those toxicologists who have vainly spent days in the preparation of pure chemicals for the generation of this gas. The method which we have to propose has been suggested by the use of Gautier's process, and some portions of our method may be considered simply

* Bulletin de la Société chimique, 24, 250.

as modifications of his, while the method as a whole has to recommend it the following features: extreme accuracy, great delicacy, and the use of but three chemicals: nitric acid, sulphuric acid and zinc.

I.—*Method for the Complete Extraction of Arsenic from Organic Matter.*

Gautier's method of destroying the organic matter is based upon the older methods of Orfila* and Filhol,† consisting of successive oxidations with nitric and sulphuric acids at elevated temperatures. The first part of our process is practically the same, except that we use a much lower temperature.

100 grams of the suspected material, cut into small pieces, are placed in a porcelain casserole of 600 cc. capacity and provided with a stirring rod of stout glass 23 cc. of pure concentrated nitric acid are added, and the dish placed on a small air-bath‡ provided with a thermometer and a single Bunsen burner. The mixture is now heated at 150–160° C., with occasional stirring. At first the tissue takes on a yellowish color, then swells up somewhat, becoming finally quite thick; soon changes again, becoming liquid, and then generally requires heating from 1½ to 2 hours, the temperature sometimes being raised to 180° C.

At this point the mass, being now quite thick again, usually takes on a deeper yellow color or orange shade. When this change of color is noticed the casserole is taken from the bath and 3 cc. of pure concentrated sulphuric acid added and the mixture stirred vigorously. The addition of concentrated sulphuric acid to the viscid residue rich in nitric acid and nitro-compounds naturally gives rise, especially at this temperature, to a considerable commotion: the mass becomes brown, swells up, nitrous fumes are copiously evolved, immediately followed by dense white fumes of suffocating odor, while the residue in the dish is changed either into a dry carbonaceous mass or a black, sticky, tar-like mass. Although the oxidation is so powerful, no deflagration takes place, and the carbonization is effected in this manner without the volatilization of any arsenic. The casserole is again placed on the bath and heated

* Traité de Toxicologie, 1, 494. Paris, 1852.

† Thesis. Paris, 1848.

‡ For air-bath we use an ordinary flat-bottomed tin basin, 7 inches in diameter, 3 inches deep, with a cover provided with an opening 5 inches in diameter. This bath is set in an iron ring fastened to a stout lamp-stand, while the end of the thermometer passes through a small hole near the edge of the cover a short distance into the bath, so that the temperature can be regulated.

for a few minutes at 180° C., then, while still on the bath, 8 cc. of pure concentrated nitric acid are added drop by drop with continual stirring, the object being, as Gautier says, to destroy more completely the organic matter, and at the same time the nitric acid falling drop by drop on the carbonaceous residue tends to prevent the formation of sulphurous acid and the consequent formation of insoluble arsenious sulphide.

After the addition of the nitric acid the dish is heated at 200° C. for fifteen minutes, and when cold a hard carbonaceous residue is the result, entirely free from nitric acid. In working with different kinds of tissue, slight deviations from the above description will frequently be observed. When much bony matter is present the last residue takes on a somewhat different character, owing to the presence of calcium sulphate, and occasionally when the 3 cc. of sulphuric acid are added the oxidation does not at once take place, but requires a little longer heating on the air-bath. But when such is the case the mixture needs constant watching in order to remove the dish from the bath at the first approach of the oxidation.

The arsenic now exists as arsenic acid, readily soluble in water. The carbonaceous residue is thoroughly extracted with boiling water, and in order to avoid all loss is not previously pulverized, but the casserole in which the oxidation took place is filled with water and heated on the water-bath for several hours. The hard mass soon softens, and by repeated treatment in this manner readily gives up all its arsenic to the aqueous solution; it is, however, better to have the carbonaceous residue in contact with different portions of warm water for about 24 hours to insure the complete extraction of the arsenic.

The reddish brown fluid containing some organic matter and arsenic acid is now evaporated on the water-bath to dryness, care being taken that the entire residue is finally obtained in one casserole. This residue* of organic matter and arsenic is dissolved

* When the residue left by the evaporation of the water is quite large, it is sometimes better to reoxidize it. This is quickly accomplished by adding a few cubic centimeters of concentrated nitric acid to the contents of the casserole and heating on the air-bath at 150–180° C. until a reddish solution is obtained. Then 3–5 cc. of concentrated sulphuric acid are added and the mixture heated at the above temperature until the nitric acid is completely driven off. The thin black fluid is then carefully mixed with the requisite quantity of No. 2 acid, shortly to be described, and introduced into the Marsh apparatus. Frequently quite a heavy, flocculent precipitate separates from the sulphuric acid solution. This does not interfere, but is poured, together with the fluid, directly into the receiving bulb, which is purposely provided with a delivery tube of large calibre.

in a definite quantity of a dilute sulphuric acid with the aid of gentle heat, and in that form, or, as frequently happens, in the form of a fluid with organic matter in suspension, is introduced into the Marsh apparatus in the manner about to be described and the arsenic weighed in the metallic state.

The following results show the accuracy of the method:—

Quantity of Arsenic introduced.	Wt. of Metallic Arsenic found.	Theoretical Wt. Metallic Arsenic.
100 grams beefsteak with .004 gram As_2O_3	.00300	.00303
" " " .004 "	.00300	.00303
" " " .004 "	.00290	.00303
" " " .003 "	.00219	.00227
" " " .005 "	.00369	.00378
" " " .005 "	.00372	.00378

Thus, from the evidence here afforded, we have a method for the determination of arsenic which is extremely accurate, and, above all other things, a method which requires but three chemicals, none of which are extremely difficult to obtain pure, and this for medico-legal purposes is a desideratum long wished for.

II.—*On the Marsh Apparatus.*

There is no method for the detection of arsenic which promises better results, either qualitatively or quantitatively, for toxical purposes, than the decomposition of arsenuretted hydrogen by heat. Indeed, no other method allows of the accurate detection of such minute quantities as the method of Marsh if properly conducted. In making use of this method as a test for arsenic in the usual manner no particular precautions have been taken to have all of the arsenic deposited in the heated tube, and in the qualitative tests for which this method has hitherto been generally used it is well known that the gas is only partially decomposed, and thus it has come to be the general impression that arsenuretted hydrogen is only partially decomposed by heat. The explanation of many poor results which have been obtained by decomposing arsenuretted hydrogen, formed from a known quantity of arsenious oxide, by heat and weighing the metallic arsenic, is not at all difficult. Otto* in describing some experiments on this point states that with 10 milligrams of arsenious oxide he sustained a loss of .8 milligram the tube being heated by two lamps and the length of the experi-

*Anleitung zur Ausmittelung der Gifte, 1875, 122.

ment 1½ hours, while the arsenic was introduced in quantities of 1 milligram; but in those experiments in which the arsenic was introduced more rapidly and the time of the experiment shortened, the results were very much poorer.

Dr. Draper* in describing a new method for the determination of arsenic based on the decomposition of arsenuretted hydrogen by heat, proved experimentally that a rapid current of arsenuretted hydrogen passed through a tube heated at five different points by single Bunsen burners was not entirely decomposed, as was evinced by the presence of five distinct mirrors; but when the evolution of gas was very slow, the arsenic was nearly all stopped by the first burner. Thus the cause of the whole trouble, which is almost entirely a mechanical one, lies in the too rapid and irregular evolution of gas, the too rapid and irregular addition of the arsenical mixture, and insufficient length of heated tube.

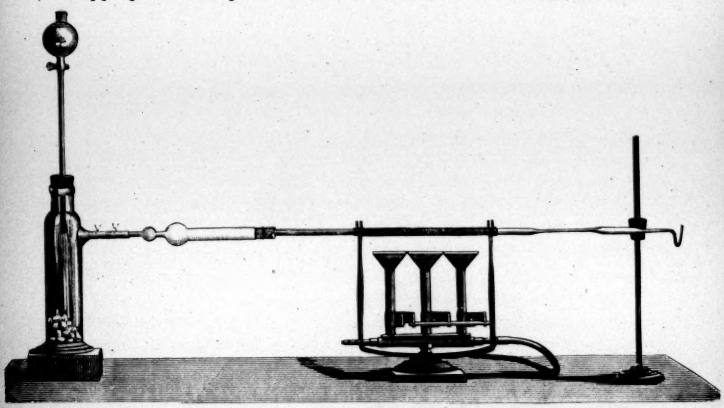
Gautier† in his recently described process for determining arsenic by the decomposition of arsenuretted hydrogen, has devised an improved arrangement for controlling the evolution of gas, by slowly introducing the arsenic mixed with a definite quantity of dilute sulphuric acid of known strength, later adding the same quantity of a stronger acid, and lastly a still stronger acid; the increasing strength of acid added counteracting the diluting effect of the reaction, so that the strength of acid remains about the same during the entire process of 2½ to 3 hours in the determination of .005 gram of arsenious oxide. Gautier decomposes the gas by passing it through a tube heated with red coals for a distance of 20-25 centimeters.

In making use of the Marsh apparatus according to Gautier's plan, we have so modified it at the suggestion of Prof. S. W. Johnson that it now appears to combine all the essentials of a perfect apparatus.

The flask, a Bunsen's wash-bottle of 200 cc. capacity, is provided with a small separating funnel of 65 cc. capacity, with glass stop-cock. This is a very material aid to the obtaining of a slow and even evolution of gas, a very important desideratum when all loss is to be avoided; for with only a funnel tube, every time a small portion of fluid is added a sudden rush of gas takes place, with probably a small but still more or less appreciable loss. But the separating funnel filled with the acid mixture can be so arranged

*American Chemist, 2, 456. † Bulletin de la Société chimique, 24, 258.

as to give a constant and regular supply of fluid at the rate of two or three drops per minute, more or less. The gas generated is dried by passing through a calcium chloride tube, and then passes through a tube of hard glass, heated to a red heat by a miniature furnace of three Bunsen lamps with spread burners, so that a continuous flame of six inches is obtained, and with a proper length of cooled tube not a trace of arsenic passes by. The glass tube where heated is wound with a strip of wire gauze, both ends being supported upon the edges of the lamp frame, so that the tube does not sink down when heated. The small furnace is provided with two appropriate side pieces of sheet metal, so that a steady flame is



always obtained. When the quantity of arsenic is very small the tube is naturally so placed that the mirror is deposited in the narrow portion, but when the arsenic is present to the extent of .005 gram the tube should be 6 millimeters in inner diameter, and so arranged that fully two inches of this large tube are between the flame and the narrow portion. When the quantity of arsenic is less the tube can naturally be smaller.

The acids of different strengths, and which for convenience we prepare in considerable quantities, are made as follows:

Acid No. 1.	Acid No. 2.
545 cc. pure conc. H_2SO_4.	109 cc. pure conc. H_2SO_4.
5000 cc. H_2O.	1640 cc. Acid No. 1.

Acid No. 3.	Acid No. 4.
218 cc. pure conc. H_2SO_4.	530 cc. pure conc. H_2SO_4.
1640 cc. Acid No. 1.	1248 cc. H_2O.

25–35 grams of granulated zinc previously alloyed with a small quantity of platinum are placed in the generator, and everything being in position, the apparatus is filled with hydrogen by the use of a small quantity of acid No. 2. After a sufficient time has elapsed the gas is lighted at the jet and the glass tube heated to a bright redness. The arsenical solution in concentrated form is mixed with 45 cc. of acid No. 2, and the mixture passed into the separating funnel, from which it is allowed to flow into the generator at such a rate that the entire fluid is introduced in one hour or one hour and a half; 40 cc. of acid No. 3 are then added and allowed to flow slowly into the generator, and lastly 45 cc. of acid No. 4. The amount of time required will vary with the amount of arsenic: 2–3 milligrams of arsenic will require about two to three hours for the entire decomposition, while 4–5 milligrams will need perhaps three to four hours. Where the amount of arsenic is small only 25 grams of zinc are needed, and but 45 cc. of acid No. 2, 30 cc. of acid No. 3, and 30 cc. of acid No. 4; but when 4–5 milligrams of arsenic are present it is better to take the first mentioned quantities of zinc and acids.

The arsenic being thus collected as a large or small mirror of metal, the tube is cut at a safe distance from the mirror, so that a tube of perhaps 2–6 grams weight is obtained. This is carefully weighed and then the arsenic removed by simple heating; or if the arsenic is to be saved as in a toxical case, dissolved out with strong nitric acid. The tube is then cleaned, dried and again weighed, the difference giving the weight of metallic arsenic, from which by a simple calculation the amount of arsenious oxide can be obtained. The results are exceedingly satisfactory, as is shown by the following, which were obtained by introducing definite quantities of arsenious oxide in the form of a solution mixed with 45 cc. of No. 2 acid, etc.

Quantity of Arsenic introduced.	Wt. of Metallic Arsenic found.	Theoretical Wt. of Metallic Arsenic.
.005 gram As_2O_3	.00373	.00378
.005 " "	.00370	.00378
.004 " "	.00300	.00303
.002 " "	.00151	.00151

In order to ascertain how delicate the detection of arsenic by

this form of apparatus is, the following tests were made, using carefully prepared standard solutions of arsenious oxide and accurately graduated burettes.

Quantity of Arsenic introduced.			
.0001	gram	As_2O_3	distinct mirror.
.00001	"	"	" "
.000001	"	"	" "
.0000001	"	"	no mirror visible.

Thus we have the $\frac{1}{1000}$th of one milligram of arsenious oxide as the smallest quantity to be detected by this form of the Marsh apparatus.

Wormley* finds the limit when the amount of fluid is small and the apparatus likewise small, $\frac{1}{20000}$th of one grain of arsenious oxide, which is equal to .0000012$\dot{9}\dot{6}$ gram of arsenious oxide. That .000001 gram of arsenious oxide is the limit under any circumstances we have proven by taking .0000001 gram and introducing this quantity into a very small apparatus with strong acid, etc., obtaining a negative result.

III.—*Influence of Organic Matter on the Separation of Arsenic as Arsenuretted Hydrogen.*

Dr. T. D. Boeke, of Holland, in a recent paper on the detection of arsenic in organic mixtures,† says, "The admirable method of Marsh in its improved form allows the detection of the minutest trace of arsenic, even in the most complicated mixtures, but with one restriction, viz.: that the solution to be examined be wholly free from organic matter." This statement expresses the prevalent opinion in regard to the influence of organic matter on the Marsh test; but the following experiments, of which those given are but a few of the many tried, show how erroneous such an opinion is. In conducting these experiments with organic matter, after the zinc is placed in the generator, 15 drops of sweet oil are allowed to flow down the side, and this as the fluid is introduced floats on top and thereby prevents any troublesome frothing. The only other thing to be guarded against is the too rapid introduction of the acids whereby loss as well as frothing of the mixture may ensue, and secondly, the heating of the flask by the chemical reaction. If necessary this latter can be prevented by placing the generator in a glass or other dish so that a stream of cold water can continu-

*Micro-Chemistry of Poisons, 287. †Chem. News, 41, 177, 1880.

ally play about it, which will keep the flask sufficiently cool to prevent the formation of any hydrogen sulphide which might otherwise show itself in slight quantity.

The first experiments were made with urine.

Quantity of Arsenic introduced.	Wt. of Metallic Arsenic found.	Theoretical Wt. of Metallic Arsenic.
.00475 gram As_2O_3 in 50 cc. urine	.00350	.00359
.00470 " " " "	.00352	.00356
.00001 " " " "	distinct mirror.	
.000001 " " " "	" "	
.00001 " " in 250 cc. urine concentrated to 50 cc.	" "	

Thus it becomes very plain that arsenic contained in urine to the extent of .000001 gram can be detected with certainty, its organic matter not offering any appreciable hindrance.

Mayençon and Bergeret* have devised a new method for the detection of minute traces of arsenic, which they have designed especially for ascertaining the rate of elimination of arsenic by the kidneys. They introduce the urine directly into a flask in which hydrogen is being generated, and ascertain the presence of arsenic by testing the gas as it issues from the end of the tube by means of a paper moistened with mercuric chloride solution; a yellow stain on the paper showing the presence of arsenic The yellow stain is due to the formation of a compound which, according to H. Rose,† contains 1 atom of arsenic, 6 of mercury and 3 of chlorine. By means of this reaction they were able to obtain a yellow color in five minutes by introducing $\frac{1}{10}$th cc. of a fluid containing 5 grams per litre of potassium arsenate. As this amount is equivalent to but .000193 gram of arsenious oxide it cannot be considered extremely delicate, and certainly a method which is dependent entirely on a particular shade of color as an indicator of the presence of the substance looked for is hardly to be compared with such an exact method as that of Marsh. Tests were now made with organic matter in the form of extractive matter from 100 grams of tissue. A large number of oxidations of lean beef in portions of 100 grams made as already described with nitric and sulphuric acids, were extracted with boiling water, and the so obtained aqueous extract evaporated to a thick residue. To each residue from 100 grams of beef definite quantities of arsenious oxide were

* Comptes rend., 79, 118. † Handbook of Chemistry, 4, 267. Leopold Gmelin.

added in solution, then 45 cc. of acid No. 2, and this mixture introduced into the Marsh apparatus recently described.

The results are as follows:

Quantity of Arsenic introduced.	Wt. of Metallic Arsenic found.	Theoretical Weight of Metallic Arsenic.
.001 gram As_2O_3 in extract from 100 grams beef,	.00070	.00075
.001 " " " " "	.00075	.00075
.002 " " " " "	.00150	.00151
.002 " " " " "	.00150	.00151
.003 " " " " "	.00220	.00227
.003 " " " " "	.00220	.00227
.004 " " " " "	.00290	.00303
.004 " " " " "	.00290	.00303
.005 " " " " "	.00369	.00378
.005 " " " " "	.00369	.00378
.005 " " " " "	.00375	.00378
.005 " " " " "	.00375	.00378
.00001 " " " " "	distinct mirror	
.000001 gram " " " "	faint mirror	

Thus we have abundant evidence that the organic matter which is present here in considerable quantity does not interfere in the least with the recovery of the entire amount of arsenic. Naturally care must be taken that the stronger acid No. 4 does not flow into the generator too rapidly, as it may thereby produce an uncontrollable frothing; the presence of the oil, however, is sufficient to prevent frothing under proper circumstances.

VII.

ESTIMATION OF SULPHUR IN ILLUMINATING GAS BY BURNING IN OXYGEN.

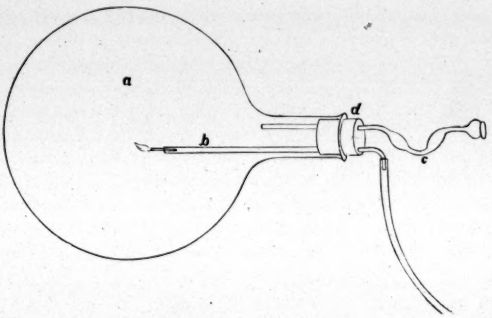
By W. G. Mixter.

The well known method of Letheby and of the Referees and the more recent way of Silliman and Sadtler*, for determining sulphur in gas, are well adapted for finding the average amount during a day, but the apparatus required by any of these methods is not commonly found in laboratories; hence the following method is brought to the attention of chemists who may have to make occasional estimations of sulphur in gas. The method is novel only in

*American Chemist, March, 1877.

the manner of the combustion, for Sauer* proposed burning illuminating gas with oxygen in a glass tube and passing the products through a hydrochloric acid solution of bromine. He, however, gave no test results.

The vessel *a* of the figure may be either a 15 litre flask, a large demijohn, or better a carboy. It is filled with oxygen† free from sulphur, rinsed with distilled water, loosely corked, and supported on its side over a sink so that a stream of water may be run over it. Or it may be floated in a tub of water and kept cool by pouring water over it. The jet tube *b* is tipped with a roll of platinum foil. The safety tube has at *c* a drop or two of water, which should not resist a water pressure of more than a quarter of an inch. The stopper *d* may be of rubber which has been



cleansed with hot potash or a cork. The gas is best measured by a small dry meter which indicates a thousandth of a foot. The gas should flow rapidly through the supply pipes for some time before testing, as well as during the test, so as to get a fair sample of the gas in the mains. When ready for the combustion the gas is lighted at the platinum tip and burned freely till all air is displaced from the meter, then the flame is made quite small, and when the index on the thousandths scale of the meter reaches 0, the jet is introduced into the flask *a*. The meter is then read and the flame is slowly increased. At first a few bubbles of gas

* Fres. Zeit. XII, 32.

† Oxygen from potassium chlorate and manganese oxide should stand over water some hours before using.

escape at *c*, and later, air passes in, provided the flask is well cooled. As soon as the gas burns much more dimly than in the air it is turned off, and the apparatus is placed upright and a few drops of bromine are poured in through the tube *c*. The cork and tubes may be removed and the neck of *a* closed with a glass plate. After the cloud which the bromine produces has completely subsided, the flask is rinsed three or four times with just sufficient water to thoroughly wet the sides. The washings are evaporated to small bulk, filtered, and the sulphur is precipitated and weighed as barium sulphate. Ordinary illuminating gas requires about one and a half times its volume of oxygen for its combustion by this method.

Test experiments were made by burning successively 0.3 and 1 cubic foot of coal gas. The duplicate results agreed closely on most days, and a variation of one grain of sulphur in 100 feet of gas was rarely found. But such results are no proof of the accuracy of the method, as illuminating gas is liable to sudden variations in composition; hence the following experiments were made. Weighed quantities of purified carbon disulphide in a sealed bulb were placed in the tube *b*, and a jet of hydrogen was burned in 13 litres of air. During the combustion of the hydrogen the bulb containing the carbon disulphide was broken. The experiments were completed in the way already described. The hydrogen used was purified by long contact with a strong solution of potassium permanganate, and when burned in an air-filled flask gave no reaction for sulphur.

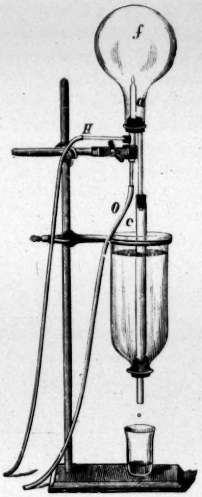
Carbon disulphide taken	0.0772	0.0631 gram
Sulphur found	84.10	84.02
Theory requires	84.21 per cent. of sulphur.	

A Synthesis of Water for a Lecture Experiment.

Hofmann* shows the synthesis of water by burning oxygen and hydrogen in a small platinum retort, and condensing the steam in a cooled spiral. The writer has used for the past two years an apparatus similar in principle, which may be made to yield 1 cc. of water a minute, and which can be put together of cheap and common laboratory apparatus. The figure and directions for making the experiment will make clear the construction of the apparatus. The thin flask *f* is removed and the hydrogen and oxygen turned on and ignited at the end of the compound blowpipe *a*, and the flame is made

* Berich. d. deutsch. chem. Gesell. 1879, 1122.

small; the flask *f* is then placed in position, and as soon as the condensed moisture is driven by the heat from the upper half of it the flame is increased. The steam condenses in the cooling tube *c*. When a few drops of water have collected in the beaker, the latter may be held up against the delivery tube, so that the gas passing out shall bubble through the water, and the flow of either gas changed until little or no gas escapes through the water. The volumes of the hydrogen and of the oxygen may now be marked on the gas holders, and at the close of the experiment it will be seen that approximately two volumes of hydrogen and one of oxygen have been consumed. The experiment requires no attention during its progress if the supply of the gases is constant. No precaution is necessary unless the flame is accidentally extinguished, in which case the flask *f* should be filled with air by blowing into it to make sure before putting it over the jet again that it does not contain an explosive hydrogen mixture.

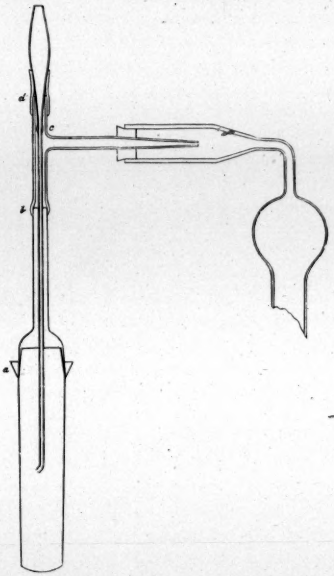


A TUBULATED CRUCIBLE FOR USE IN ESTIMATING VOLATILE PRODUCTS OF IGNITION.

By F. A. Gooch.

In many processes of analysis which involve the collection and direct estimation of volatile products of ignition (such, for example, as the determination of carbon in irons and steels, or of carbon and hydrogen in organic compounds), the use of combustion tubes of glass or porcelain or platinum, either with or without boats of platinum or porcelain as accessories, in connection with proper

absorption apparatus, is attended with satisfactory results; but accuracy in processes of this kind which require the application of high temperatures, particularly when the substance under examination is submitted to ignition in contact with a flux or other reagent (as, for instance, in Lipöcz's method of determining the water of constitution of silicates by fusion with sodic carbonate) is not easily secured. It is for use in such processes that the appa-



ratus whose description is appended was devised. Its practical working has been found to be satisfactory, its management easy, and the results of analysis accurate. Its range of applicability to processes, both actual and prospective, whose object is the determination of volatile products of ignition, promises to be extensive.

A platinum crucible shaped, as shown in the figure, in the form of two truncated cones placed base to base, has its upper rim folded

twice upon itself so as to present a smooth conical surface on the exterior and an up-turning flange. A conical cap of platinum prolonged upward in a tube fits the outer surface of the crucible near the flange, *a*, in a ground joint. Over the upper end, *b*, of the platinum tube one end of a T tube of lead glass is fused, and the other end of the same branch of the T tube is connected by means of a piece of rubber tubing, *d*, with a glass tube into whose lower end, *c*, is fused a slender platinum tube which extends downward into the crucible and terminates in a slight turn to one side; or, in special cases in which the use of a rubber joint is not permissible, the connection between the inner and outer tubes may be made by fusing the slender platinum tube directly into the upper end of the T tube. The horizontal branch of the T tube is drawn out a little and passes through the stopper of an absorption tube, as shown in the figure. An air-tight joint is made between the cap and the crucible by melting into the flange some easily fusible material like the neutral anhydrous sodic tungstate, or sodic metaphosphate, the former being preferable in most cases; but the seal may be varied, of course, according to the nature of the case in hand.

In using the apparatus the substance to be ignited is put into the crucible, the cap is adjusted, the inner tube set in place and the rubber joint made, the horizontal branch of the T tube connected with the absorption apparatus, the opening in the upper end of the inner tube closed by a cap made of rubber tubing stoppered with a bit of glass rod, and finally the seal melted into the flange with a blowpipe-flame.

As the apparatus now stands it should be air-tight. Next, the cap is removed from the top of the inner tube, and the latter connected with an arrangement for forcing (or drawing) pure air or other gas, according to the purpose of the experiment, through the crucible and absorption tubes, and heat is applied to the crucible. The temperature may be raised until the lower part of the crucible shows a white heat without fusing the seal of sodic tungstate within the flange.

To take the apparatus to pieces after the completion of the operation it is only necessary to disconnect the absorption apparatus, remove the inner tube, remelt the seal and lift the cap. Hot water removes the adhering sodic tungstate very easily.

Some of the dimensions of the particular apparatus which I have in use are as follows:—*

Capacity of crucible	22. cm^3.
Diameter of crucible at top	1.6 cm.
" " " flange	1.9 "
" " " bottom	1.7 "
Height of crucible without cap	9. "
" " tube above cap	5. "
Diameter " " "	0.6 "
Length of inner tube of platinum	13. "
Diameter " " "	0.2 "
Weight of platinum in apparatus	48 grams.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

By C. Loring Jackson.

V.

ON PARAIODBENZYL COMPOUNDS.†

C. F. Mabery.

The preparation of *paraiodbenzylbromide*, $C_6H_4ICH_2Br$, has been described in the first article of this series;‡ but the method there given did not invariably yield good results, the product often being mixed with a black tar which it was very hard to remove completely by crystallization. A more careful study of the conditions of the reaction has shown that this was due to an oily impurity

* The platinum parts of the apparatus were most skillfully made by Mr. J. Bishop, of Sugartown, Chester Co., Pa. I take this opportunity, too, to call attention, incidentally, to the fact that Mr. Bishop makes a very convenient form of perforated crucible—conical in shape and provided with a cap fitted to the bottom, after a design by Mr. A. A. Blair—intended for use in the process of filtration described by me in this Journal, Vol. I, page 317.

† Proceedings American Academy of Arts and Sciences. Communicated by the Authors.

‡ This Journal, Vol. I, p. 103.

of the iodtoluol, a very small amount of which was sufficient to destroy a great part or even the whole of the paraiodbenzylbromide: if the paraiodtoluol purified by distillation was carefully pressed between filter-paper, this oil was absorbed, and then the product of the bromiring was nearly white after the first crystallization.

The following substances were obtained from paraiodbenzylbromide by the usual metathetical reactions:

Paraiodbenzylalcohol, $C_6H_4ICH_2OH$, was prepared from the product of the action of sodic acetate on the bromide, by heating it to 160° with aqueous ammonia in a sealed tube: the solid thus obtained was purified by pressing between filter-paper, and crystallization from carbonic disulphide. It was also made* by boiling paraiodbenzylbromide with water for several hours in a flask with a return-condenser. That hydrobromic acid was set free was proved by the acid reaction of the water, and the precipitate of argentic bromide formed on adding argentic nitrate to it, after the organic matter had been removed.

The alcohol prepared according to the first method was analyzed.

0.2508 gr. substance gave 0.3260 gr. CO_2 and 0.0633 gr. H_2O.

	Calculated for C_7H_8IOH.	Found.
Carbon	35.89	35.45
Hydrogen	2.99	2.79

Properties.—It crystallizes from carbonic disulphide or alcohol in small silky white scales; from boiling water, in long needles, with an aromatic odor like that of the corresponding bromine compound, and no action on the eyes; melting-point, 71¾°; very slightly soluble in cold, somewhat more soluble in hot water; freely in alcohol, ether, benzol, and carbonic disulphide.

The *paraiodbenzylacetate* was not obtained pure, because, on account of its instability, a great quantity of substance would have been consumed in its preparation; and it did not seem worth while to sacrifice the large amount of time necessary to prepare so much paraiodbenzylbromide, especially as its decompositions seemed analogous to those of the more accessible parabrombenzylacetate, which will be studied in this laboratory. The following account of the attempts to prepare it is, however, given, as it throws some light upon the nature of the substance. The first difficulty encountered was due to the fact that the sodic acetate only partially decomposed

* This Journal, Vol. II, p. 88.

paraiodbenzylbromide. The two substances were boiled with absolute alcohol, and an oily product obtained, which solidified at 0°, and after crystallization from alcohol melted at 45°: the results of an analysis of this substance are given under I; it was then heated once more with sodic acetate and absolute alcohol, and the result analyzed, when the numbers given under II were obtained.

I. 0.4007 gr. substance gave 0.4416 gr. CO_2 and 0.0909 gr. H_2O.

II. 0.2936 gr. substance gave 0.3403 gr. CO_2 and 0.0738 gr. H_2O.

	Calculated $C_7H_4IC_2H_3O_2$.	Found. I.	Found. II.	Calculated C_7H_4IBr.
Carbon	39.12	30.05	31.61	28.28
Hydrogen	3.26	2.52	2.79	2.03

These numbers seem to show that the substance was nothing more than a mixture of the acetate and bromide, and this conclusion is strengthened by the fact that it attacked the eyes like the bromide. In order to obtain the acetate from this mixture it would have been necessary to use fractional distillation, which had been found, in the case of parabrombenzylacetate, to cause almost complete decomposition: it was therefore thought better to try to decompose the paraiodbenzylbromide completely by using argentic, instead of sodic, acetate. In this case the product was an oil, which showed no signs of solidification, even after standing in an open watch-glass for some time. The term then came to an end, and it remained exposed to the air during the summer vacation of three months, at the end of which time the watch-glass contained a solid residue, which was proved to be paraiodbenzoic acid by its melting-point and the following analysis of its silver salt:

0.2185 gr. substance gave by precipitation with hydrochloric acid 0.0857 gr. AgCl.

	Calculated for $C_6H_4ICO_2Ag$.	Found.
Silver	30.42	29.62

The formation of this acid under these conditions can be explained by the supposition that the acetate absorbed water from the atmosphere and became converted into the alcohol, which was then oxidized by exposure to the action of the air; and this view is supported by the observation, that a product from the reaction of paraiodbenzyl bromide on sodic acetate dissolved in ordinary alcohol, when precipitated by water, and the oil thus obtained allowed to stand exposed to the air in a watch-glass, deposited crystals, which upon recrystallization melted at 70°, and were, therefore, the alcohol.

It must, however, be remembered that this oil contained some of the bromide, and that the alcohol may have been formed from this instead of the acetate. This conversion of the acetate into the alcohol or acid seemed likely to render its purification so difficult that the experiment with argentic acetate was not repeated. A similar formation of the substituted benzoic acid has been observed in the attempts to purify parabrombenzylacetate.

Paraiodbenzylcyanide, $C_6H_4ICH_2CN$, was obtained by boiling the bromide with alcoholic potassic cyanide, precipitating with water, and crystallizing from alcohol. Its composition was established by the following nitrogen determination:

0.3523 gr. substance gave 17.83 cc. nitrogen, under a pressure of 736 mm. and at the temperature 23°.

	Calculated for C_7H_6ICN.	Found.
Nitrogen	5.76	5.67

Properties.—White plates with a pearly lustre, characteristic odor, and no action on the eyes; melting-point, 50½°; insoluble in water; readily soluble in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid.

Paraiodalphatoluic acid, $C_6H_4ICH_2COOH$, was obtained by heating the cyanide with fuming hydrochloric acid to 100° in a sealed tube; after four hours, the liquid on cooling became filled with flattened needles, which were purified by crystallization from boiling water. The composition of the acid was fixed by the analysis of its silver salt.

Properties.—Narrow, tapering, white plates, often over two centimeters long, with an agreeable odor resembling that of sweet alyssum; melting-point, 135°; sublimes in branching needles at a somewhat higher temperature; but slightly soluble in cold, readily in hot water, and in alcohol, ether, benzol, carbonic disulphide, and glacial acetic acid. A mixture of potassic dichromate and dilute sulphuric acid oxidizes it, forming paraiodbenzoic acid, which was recognized by its high melting-point. It is freely soluble in aqueous ammonia, but the ammonium salt could not be obtained in the solid state, as evaporation of the solution, whether on the water-bath or *in vacuo*, at ordinary temperatures, decomposed it, leaving the acid, which was recognized by its sparing solubility in cold water and its melting-point of 135°.

Argentic paraiodalphatoluate, $C_6H_4ICH_2COOAg$, was made

by adding the solution of the acid in ammonia water, from which the excess of ammonia had been driven off by warming on the water-bath, to argentic nitrate: the white curdy precipitate was washed, dried *in vacuo*, and analyzed.

0.7065 gr. substance, dissolved in dilute nitric acid and precipitated with hydrochloric acid, gave 0.2701 gr. of argentic chloride.

0.1214 gr. substance gave 0.0475 gr. of argentic chloride.

	Calculated for $C_8H_6IO_2Ag$.	Found. I.	II.
Silver	29.27	28.78	29.45

Properties.—A white curdy precipitate resembling argentic chloride, sparingly soluble in boiling water, from which it crystallizes in lustrous plates; readily soluble in dilute nitric acid. The dry salt is only slightly blackened by heat and light.

Baric paraiodalphatoluate, $Ba(C_6H_4ICH_2COO)_2 \cdot H_2O$, prepared by neutralizing baric hydrate with a hot aqueous solution of the acid, and evaporating to crystallization, gave the following results on analysis:—

0.5400 gr. substance dried *in vacuo* lost, when heated to 100°, 0.0153 gr., and gave 0.1881 gr. $BaSO_4$.

	Calculated $Ba(C_8H_6IO_2)_2 \cdot H_2O$.	Found.
Water	2.66	2.83
Barium	20.23	20.48

It forms microscopic white needles, easily soluble in water.

The *calcium salt*, made by treating calcic carbonate with a concentrated aqueous solution of the acid, was also freely soluble in water, and crystallized in slender branching needles.

The solution of the ammonium salt of the acid obtained by dissolving it in aqueous ammonia, and driving off the excess of ammonia on the water-bath, behaved as follows with various reagents:

With *cupric sulphate*, pale bluish-green flocks, insoluble in water, but soluble in acids.

With *ferric chloride*, pale yellowish-brown flocks, insoluble in water.

With *chromic chloride* or *nickelous nitrate*, a green precipitate.

With *cobaltous nitrate*, a pink precipitate.

With *plumbic acetate*, *mercurous nitrate*, or *aluminic chloride*, a white flocculent precipitate.

With *zincic* and *manganous nitrate*, salts which are sparingly

soluble in water and crystalline; the manganese salt is flesh-colored. No precipitate was obtained with salts of *cadmium*, *magnesium*, *strontium*, and the *alkaline metals*. In general, its salts resembled very closely those of the corresponding parabromalphatoluic acid.

Paraiodbenzylsulphocyanate, $C_6H_4ICH_2SCN$, was made by boiling an alcoholic solution of potassic sulphocyanate with paraiodbenzylbromide: the oil obtained by precipitating the product with water solidified upon cooling, and was purified by draining on filter-paper, and crystallization from hot alcohol.

0.3661 gr. substance gave 0.4702 gr. CO_2: the water was lost by breaking the chloride of calcium tube.

0.2159 gr. substance gave, according to Carius, 0.1844 gr. baric sulphate.

	Calculated for C_7H_6ISCN.	Found.
Carbon	34.91	35.02
Sulphur	11.64	11.72

Properties.—It crystallizes from alcohol in long white lustrous plates which are often twinned; it has a slight but disagreeable odor, like that of the benzylsulphocyanate; melting-point, 40¼°; insoluble in water; slightly soluble in cold, more so in hot alcohol, freely in ether, benzol, carbonic disulphide, and glacial acetic acid.

Paraiodbenzylamines.

Alcoholic ammonia removed the bromine from the paraiodbenzylbromide with great ease: in fact, it was only necessary to warm the substances together in a flask to obtain a voluminous white precipitate consisting of the secondary and tertiary amines. If a more dilute solution was used, the tertiary amine alone was deposited; while a mixture of this and the secondary amine fell upon adding water. The liquid decanted from this precipitate was evaporated to dryness, and the residue separated by treatment with water into an insoluble bromide of the secondary and the soluble bromide of the primary amine. The mixture of the secondary and tertiary amines, after thorough washing with water, was treated with hot alcohol, which separated without difficulty the more soluble secondary from the but slightly soluble tertiary amine.

Triparaiodbenzylamine, $(C_6H_4ICH_2)_3N$, was purified by recrystallization from ether, dried *in vacuo*, and analyzed.

I. 0.3609 gr. substance gave 8.08 cc. nitrogen, under a pressure of 745.6 mm. and at the temperature 20°.

II. 0.8461 gr. substance gave 21.08 cc. nitrogen, under 742.8 mm. and at 21°.

	Calculated for $(C_7H_6I)_2N$.	Found. I.	II.
Nitrogen	2.15	2.51	2.76

Properties.—White needles arranged in groups resembling hour-glasses, with an agreeable odor; melting-point, 114½°; is turned gray by heating, and the melting-point is then much higher; insoluble in water and cold alcohol; very slightly soluble in boiling alcohol, easily in ether, benzol, and carbonic disulphide. A chloride could not be obtained by treating a solution of the base with hydrochloric acid.

Triparaiodbenzylamine chlorplatinate, $[(C_6H_4ICH_2)_3NH]_2PtCl_6$, appeared as a bulky yellow precipitate, on adding a solution of platinic chloride to the amine dissolved in ether. It was washed with alcohol, dried *in vacuo*, and analyzed:

0.7812 gr. substance gave on ignition 0.0886 gr. platinum.

	Calculated for $[(C_7H_6I)_2NH]_2PtCl_6$.	Found.
Platinum	11.32	11.34

Yellow needles nearly insoluble in water and alcohol.

Diparaiodbenzylamine, $(C_6H_4ICH_2)_2NH$, was purified by repeated recrystallization from hot alcohol, dried *in vacuo*, and analyzed.

0.4050 gr. substance gave 12.33 cc. nitrogen, under a pressure of 763.8 mm. and at the temperature 25.5°.

	Calculated for $(C_7H_6I)_2NH$.	Found.
Nitrogen	3.12	3.40

Properties.—White needles with square ends, having an odor somewhat resembling that of the nitrile; melting-point, 76°; insoluble in water; sparingly soluble in cold, freely in hot alcohol, and in ether, benzol, and disulphide of carbon.

The *chloride of the base*, obtained by adding hydrochloric acid to its alcoholic solution, crystallizes in thick, white plates, with a very high melting-point; nearly insoluble in water, slightly soluble in alcohol and benzol, freely in carbonic disulphide and glacial acetic acid. It was proved to be the chloride, by treating its nitric acid solution with argentic nitrate, when argentic chloride was precipitated.

The *bromide of the base* was formed under certain conditions

during the preparation of the amines: it was purified by crystallization from alcohol. Short, thick, pointed, white prisms, with a pearly lustre, and a high melting-point; insoluble in water; somewhat soluble in alcohol, more so in ether, benzol, and carbonic disulphide; sparingly soluble in glacial acetic acid. It was proved to be the bromide of the diamine, by treating it with a solution of sodic hydrate, when a base was set free, melting after recrystallization from boiling alcohol at 76°; while bromine was detected in the sodic hydrate by the usual test with chlorine water and carbonic disulphide.

Diparaiodbenzylamine chlorplatinate, $[(C_6H_4ICH_2)_2NH_2]_2PtCl_6$, was obtained as a yellow precipitate on adding platinic chloride to an alcoholic solution of the base: it was washed with alcohol, dried *in vacuo*, and analyzed.

0.3951 gr. substance gave on ignition 0.0609 gr. platinum.

	Calculated for $[(C_7H_6I)_2NH_2]_2PtCl_6$.	Found.
Platinum	15.07	15.42

Properties.—Pale yellow microscopic crystals, grouped like certain forms of frost, almost insoluble in water and alcohol.

Monoparaiodbenzylamine, $C_6H_4ICH_2NH_2$, was most easily obtained by heating paraiodbenzylbromide to 120° in a sealed tube with alcoholic ammonia. The bromide of the primary amine was dissolved out of the product with water, and after treatment with sodic hydrate the free base was extracted with ether. It is an oil which absorbs carbonic dioxide from the air and passes into the *carbonate*, a white crystalline substance melting at 113°.

The *chloride* formed by dissolving the carbonate in hydrochloric acid, crystallizes in slender white needles, which melt at 240°, and are readily soluble in water or alcohol, sparingly in ether.

Monoparaiodbenzylamine chlorplatinate, $[C_6H_4ICH_2NH_3]_2PtCl_6$, was made from the chloride by addition of chlorplatinic acid, and purified by washing with alcohol. It gave the following result on analysis:

0.3560 gr. of the salt gave 0.0795 gr. of platinum.

	Calculated for $(C_7H_6INH_3)_2PtCl_6$.	Found.
Platinum	22.47	22.34

CHLORO-NITRO-PHENETOL.

By Edward J. Hallock.

Monochlorophenetol was first prepared by Henry* in 1869, by the action of phosphorus pentachloride upon phenetol. Five years later Beilstein and Kurbatow† made both the ortho- and parachloro-phenetols from chlorophenol. The latter was probably identical with Henry's chlorophenetol. A more convenient and economical method of its preparation is by acting upon phenetol with potassic chlorate and hydrochloric acid. Several test tubes containing each 5 cc. of phenetol and two or three grams of pulverized potassic chlorate were placed in the draught hood, and a few drops of acid added to each. When the action, which is very energetic, had somewhat subsided, more acid was added until all the chlorate had been decomposed. On pouring into water the resulting product sinks as a heavy yellow oil beneath the water. On distilling a violent bumping usually takes place when the thermometer reaches 100°. After this the thermometer rises rapidly to 200°, and nearly all of the liquid distills over below 240°, where partial decomposition takes place. The distillate remains liquid at ordinary temperatures.

On treating the chlorophenetol thus obtained with nitric acid (concentrated but not fuming), it is attacked quite energetically and converted into a nitro-compound, which is at first oily, but when washed with water soon solidifies to a mass of light yellow crystals, insoluble in water but readily soluble in alcohol and ether. Analysis showed it to be a mono-chloro-mono-nitrophenetol, $C_6H_3Cl(NO_2)OC_2H_5$. It crystallizes in beautiful white needles, resembling the paranitrophenetol described in a former number of this journal. Its fusing point is 61°, which corresponds with that of the parachloro-orthonitrophenetol obtained by Faust and Saame‡ by a much more troublesome method, viz., heating the silver salt of chloronitrophenol with ethyl iodide. These investigators mention it as possessing an unpleasant odor, which is not the case with that obtained by the above method, which also has the advantage of yielding it almost absolutely pure at first.

*Ber. d. d. ch. Ges. 2, 711. †Ber. d. d. ch. Ges. 7, 1395.
‡Zeitschr. f. chem. [2] V, 1869, 450.

The chlorophenetol obtained by the action of potassic chlorate and hydrochloric acid upon phenetol has a peculiar odor not unlike that of oil of anise.

Several attempts have been made to obtain a nitrosophenetol by means of potassic nitrite, and in other ways, but as yet without success; the phenetol is either unattacked, or a nitrophenetol is formed.

COLUMBIA COLLEGE, NEW YORK, *August* 18, 1880.

REVIEWS AND REPORTS.

BRIEF REVIEW OF THE MOST IMPORTANT CHANGES IN THE INDUSTRIAL APPLICATIONS OF CHEMISTRY WITHIN THE LAST FEW YEARS.

(*Continued from p. 150.*)

MATERIALS AND PROCESSES CONNECTED WITH CLOTHING.

General Chemical Treatment of Textile Materials.—The old fashioned method of washing wool, involving entire waste of the large amount of potassium soaps of fatty acids, fatty alcohols, and their compound ethers, which constitute the grease to be removed, has been improved on, to some extent by extraction of the fatty matter with carbon disulphide or petroleum naphtha, but yet more by the Maumené and Rogelet process for making potash, by regulated leaching of the wool, evaporation of the liquid obtained, and either at once burning off organic matter, or charring in close vessels, with utilization for illuminating purposes of the gaseous products given off.

The practice has become established of freeing wool from burs, bits of straw, or other forms of vegetable fibre, by soaking with dilute sulphuric acid, pressing out surplus liquid, and gradually heating the wool up to about 100° C., the vegetable impurities being thus so attacked that they are readily reduced to dust and mechanically removed. Solution of aluminum chloride has been used for the same purpose, as also gaseous hydrochloric acid, and mixed fabrics of wool and cotton or linen may be broken up and the wool recovered in useful form.

The advantage of using *hard* water, containing lime salts, in reeling raw silk has lately been pointed out, the amount of gelatinous matter removed in solution from the surface of the fibre being

thus diminished, and loss of tenacity and of beauty in appearance lessened.

Attention has been prominently drawn of late to the extending habit on the part of too many manufacturers of fraudulently "weighting" textile fabrics with foreign substances, introduced to give apparent density to flimsy products of the loom. Cotton and silk have been the materials chiefly treated by such objectionable methods. The sizing legitimately used upon the warp of cotton goods, to give strength and smoothness of surface to the threads in weaving, consists mainly of flour with the gluten partially altered by fermentation, with soap and fatty matter, and should not much exceed five per cent. of the weight of the finished cloth; but white porcelain clay in large quantity, magnesium chloride to attract and retain moisture, and a little zinc chloride producing the same effect and also acting as an antiseptic to obviate mildew, have been extensively employed of late years, sometimes forming altogether fifty or even sixty-five per cent. of the cloth as sold. It is reported also that magnesium sulphate from Stassfurt kieserite has been largely applied to this use, the cloth being passed through a concentrated solution of the salt and then gradually dried.

Silk goods are also notoriously "weighted" to an enormous extent, chiefly in the course of nominal dyeing, both organic and mineral materials being used, among the latter salts of lead, barium, aluminum, etc., with viscid material, such as shellac dissolved in a watery solution of borax, to produce attachment to the cloth, and hygroscopic substances to attract moisture, often with serious injury to the durability of the real fabric, which is more or less corroded and weakened. Samples are reported in which the foreign substances introduced have amounted to two-thirds of the whole weight.

Bleaching, including the Manufacture of Chloride of Lime.—Compulsory condensation of the hydrochloric acid produced in the alkali manufacture by Leblanc's process has for some years tended to fix, even more than formerly, as a regular concomitant of this industry, the production of bleaching powder.

The most important event in the history of the latter has been the really successful solution of the problem of regenerating the manganese employed in such form as to be used over again. The process first introduced for this purpose by Dunlop, although capable of being worked, has never found general acceptance, while that of Weldon has within ten years come to be very extensively, it may almost be said universally employed, and with highly satisfactory results, the loss of manganese being now reduced in well managed works to one and a half per cent., while the production of bleaching powder has within the same time increased threefold, and its price has been reduced by one-half. The process itself, consisting in precipitation of the still liquor, containing manganous chloride, by an excess of calcium hydrate, and oxidation of the precipitate by air forcibly blown for some time through it and the

liquid in which it is suspended, has been gradually improved, so that now the chief product seems to be an acid calcium manganite corresponding nearly to the formula

$$\left.\begin{matrix}\mathrm{Ca}\\ \mathrm{H_2}\end{matrix}\right\} (\mathrm{MnO_3})_2.$$

It still yields, however, large quantities of calcium chloride as a by-product, and a satisfactory mode of utilizing the chlorine thus carried off remains, as has already been noted in this report, an important desideratum. The Deacon process for making chlorine at the expense of the oxygen of the air, avoiding altogether the use of manganese, is still in use to a small extent, but has been found to involve a good deal of difficulty, especially in maintaining in a state of activity the sulphate of copper used as the means of promoting the action of atmospheric oxygen.

The conditions for the production of the best chloride of lime have become better understood, particularly the advantageous use of a considerable excess of lime, and a low temperature during the absorption of the chlorine, and the avoidance of packing the product while in too fresh and moist a state.

In the bleaching process itself there is no capital novelty to record as to the use of chlorine, but it is interesting to note the actual introduction upon an industrial, though still limited, scale of the use of hydrogen dioxide, said to be now applied with special advantage to the treatment of Indian tusseh silk. Potassium or sodium permanganate, followed by a weak acid, was also for some time used as a bleaching agent, but has been practically discarded. Atmospheric oxygen in presence of oil of turpentine has been applied to the bleaching of feathers and some other materials of animal origin. One of the most useful of modern improvements, when properly managed, seems to be the combination of chlorine and air bleaching; linen goods in particular, and some of the higher grades of cotton cloth, being satisfactorily bleached by preliminary removal of most of the color with the aid of chlorine, and completion of the process after the ancient fashion of exposure to sun and air, so as combine the rapidity of the one method with the exemption from injury to the fabric of the other.

Preparation of Dye-stuffs.—In the history of these materials five principal phases are observable. First, in the earliest times, the use of native dyes of organic origin, chiefly derived from the vegetable kingdom. Secondly, since the discovery of America and the early voyages of the fifteenth and sixteenth centuries to the west coast of Africa and to India, the use of exotic dyes, also organic. Thirdly, since the middle part of the last century, the employment of mineral dye-stuffs, such as iron buff, chrome yellow, etc. Fourthly, within the last twenty years the introduction of artificial organic colors in vast number and variety, and lastly, within but about ten years, the successful reproduction of natural organic colors by artificial means.

The changes in regard to the preparation of natural dye-stuffs have not of late been very numerous or important. A marked falling off in the production of madder, and of the various partially purified or concentrated forms in which it comes to market, such as garancine, has been the consequence of the introduction of artificial alizarine. Ammonia, instead of lime, has been applied with advantage to the extraction of indigo in Java, and in India it has been found that by using steep-water heated to 110° F. by steam, instead of water at the natural temperature of 92°–95°, an increase of product may be obtained amounting to as much as 25 per cent., the exhaustion of the plant being so complete that further steeping gives practically no more color. For sundry of the long known vegetable dyes the use of concentrated extracts prepared by exhaustion with water and evaporation to solid or pasty consistence, has to a considerable extent replaced the immediate employment of the crude wood, bark or other vegetable material; the character of these extracts, both as to solubility and tinctorial power, has undergone no small improvement.

Our knowledge of the coloring principles of several important natural dye-stuffs has been advanced, as in reference to hæmatoxyline, bresiline, indigotine and orcine; the synthesis of the latter two has been accomplished, though not yet with industrial results,* and will probably be succeeded ere long by that of the others.

Artificial Coloring Matters.—It is, however, chiefly with artificial dye-stuffs that the industrial, as well as scientific history of the last few years has been chiefly occupied. The whole of this brilliant chapter of the subject is so recent, and has attracted such general attention, that it is not easy to decide what may merit special mention as newest and most interesting.

The preliminary treatment of the coal-tar, which forms the main material with which the maker of artificial organic colors works, has become systematized, and in many of its details improved. Particularly has the management of the later stages of coal-tar distillation become better understood. Agitation of the contents of the still, distillation in a current of indifferent gas, and other modifications of practice have improved the yield of the less volatile products, especially the valuable anthracene, whose purification also is better provided for than formerly. The hydrocarbons of lower boiling points—benzene, toluene, etc.—are obtainable of much greater individual purity than some years ago, and in mixtures of more definite and uniform character adapted to the preparation of particular classes of colors. A satisfactory direction for the employment of much of the heavy coal-tar naphtha remains still to be found. Looking to a supposed probability that the supply of coal-tar may be cut short by the progress of electric illumination, Greiff has lately calculated that about 4,000,000 kilos of crude benzene are needed per annum for the production of aniline colors,

* It has been very recently reported that Baeyer has succeeded in producing artificial indigo by a commercially practicable process, the starting point of which is benzene.

and 900,000 kilos of pure anthracene for making artificial alizarine, and claims that, even should coal gas altogether cease to be made, coal might nevertheless be profitably distilled (with modification of the process) for its other valuable constituents, especially those just named, and that these (benzene, toluene and anthracene) can also be readily obtained, and in sufficient quantity, from the residues of distillation of petroleum of the Caucasus, raising the question also whether American petroleum residues have been adequately examined in this direction.

In regard to the original so-called aniline colors, one of the most important changes has been the application on the great scale of Coupier's process, or a modification of it, for making aniline red (rosaniline salts) without the use of arsenic. This process, consisting essentially in heating together in the presence of an acid nitrobenzene and commercial aniline oil of high boiling point, rich in toluidine, has been adopted by several of the largest manufacturers. The important researches of E. and O. Fischer, Rosenstiehl, and Dale and Schorlemmer, have proved that under the name rosaniline have been included both isomeric and homologous bases of generally similar character, and Dale and Schorlemmer have shown that of these para-rosaniline, with the formula $C_{19}H_{17}N_3$ (identical with that made from para-toluidine) may be prepared from phenol by converting this into aurine, $C_{19}H_{14}O_3$, and heating the latter with an excess of aqueous ammonia; while if aurine be heated with aniline the final product is tri-phenyl-pararosaniline, thus establishing full connection between phenol and the whole series of aniline colors.

The original aniline violet of Hofmann, obtained by the methylation of pre-formed rosaniline salts, has been to a large extent replaced by the "*violet de Paris*," made by first heating aniline under pressure with methyl chloride, or methylic alcohol and hydrochloric acid, thus obtaining methylated aniline derivatives, and then oxidizing such product by heating it in the air, mixed with sand and a salt of one of the heavy metals, usually cupric nitrate, to facilitate the oxidation process. Monnet, Reverdin and Noelting have lately shown that, of the mono- and di-methyl anilines and various isomeric mono- and di-methyl toluidines obtainable from commercial aniline oil in the first stage of this manufacture, pure di-methyl-aniline is the only one which can be advantageously used in the preparation of the violet, in view of adequate yield, solubility, etc., of the product. The finest phenylated blues are now made by heating together very pure rosaniline (made by Coupier's process), a large excess of pure aniline, and benzoic or stearic acid, preferably the former. Aniline green, "*vert lumière*," is now made by heating methyl salts with methyl-aniline violet, thus dispensing with the costly use of iodine. But methyl green has itself been largely replaced of late by "malachite green," made by the action of benzoyl tri-chloride on di-methyl-aniline; the color so obtained exhibiting superior stability in comparison with the

methyl and iodine greens. The soluble aniline blacks—"indulines" and "nigrosines"—have come into use for general dyeing purposes, particularly in some forms specially fit for use upon silk goods. The indulines appear to be phenylated derivatives of violaniline, while in the nigrosines phenyl has been substituted for hydrogen in the phenyl groups of the same base. The sulphonates of both are soluble in water as well as alcohol. Almost pure aniline, it has been found, is necessary for the production of these black dyes of the best quality.

Di-phenylamine has come to be largely made by heating together under pressure aniline and its hydrochlorate, and blue and green dyes of peculiar tints are manufactured from it. The hex-nitro-derivative, "aurantia," is also one of the more recently introduced dyes.

The phenol colors, picric acid, iso-purpurate of potassium, and aurine, have shared in the advantage from increased purity of commercial phenol. It has been lately proposed to make picric acid by slowly adding the sulphacid of phenol to concentrated nitric acid, the reaction proceeding slowly, and without requiring application of heat. The formula of aurine (red coralline) has been established, and the conditions of its production from phenol studied.

The beautiful resorcine derivative, eosine, is of comparatively recent introduction, and has established its claim to be considered a valuable addition to the resources of the dyer. The phthaleins of phenol, resorcine and other phenolic substances have of late been converted into eosine and analogous coloring materials by using, instead of bromine itself, a mixture of a bromide and bromate (or corresponding chlorine or iodine compounds) with acetic acid or some other weak acid; and alkaline hypochlorites have also been employed to thus modify the preparation of aureosine and other colors of the eosine class, whose beauty is unfortunately not equalled by their permanence. Methyl, benzyl, and other alcoholic radicles have also been used to form substitution products of resorcine and the colors derivable from it. The tri-atomic phenol, pyrogallol, has given rise to the dyes "galleine" and "cœruleine."

The naphthalene colors have perhaps not established and extended themselves as largely as some other classes, but the calcium or sodium compound of di-nitro-naphthol ("Martius' yellow") still retains its place among valuable dyes.

It is needless to say that artificial alizarine from anthracene has within ten years replaced to an immense extent the natural madder, and become recognized in the very front rank of artificial coloring materials. There have been important additions of late to our knowledge of the isomeric and closely related coloring substances occurring in artificial alizarine, and new nitro- and amido-derivatives of alizarine, with tinctorial properties, have been obtained, and the isomerism of these bodies in a measure worked out by the researches of Perkin, Rosenstiehl, Schützenberger, Morton and

others. Alizarine blue, a derivative of mono-nitro-alizarine, attracted for some time attention as affording the means of producing tints like those from indigo, but it proved instable on exposure to light, and has disappeared from commerce. New red, violet, and blue colors have lately been obtained from mono- and di-amido- and nitro- anthraquinone, of which some may perhaps prove permanently useful.

Beautifully colored derivatives of phenanthrene have not long since been announced.

A large class of tinctorially valuable materials has quite recently been introduced, the so-called azo-colors, produced by the reaction of di-azo-compounds upon phenols, amido-compounds, etc. The comparatively long known and permanent "Bismarck brown" consists principally of tri-amido-azobenzene. The prototype of the many recently introduced colors is "chrysoidine," the hydrochlorate of meta-di-amido-azobenzene, and it has been followed by the production of the "tropaeolines" and numerous other parallel derivatives of phenol, cresol, naphthol, resorcine, pyrogallol, &c., modified in various ways by the presence of hydroxyl, nitryl, amido-, sulphonic, and other groups. These new dyes are chiefly of yellow, orange, and scarlet red tints.

Witt has lately described toluylene blue, violet, and pink, representatives of a new class of colors obtained from diamines by simultaneous oxidation of amido- and methyl groups, and forming in a sense a connecting link between the rosaniline series and that of the azo colors.

The "Cachou de Laval" of Croissant and Bretonnière, although of undetermined and probably indefinite constitution, is a material of too much practical value to be passed over without notice. Made by heating to 250° or 300° C, in close vessels, various waste forms of vegetable fibre, such as saw-dust, spent dye-woods, rags, paper refuse and the like, with caustic alkali and sulphur, the product is obtainable of various colors, chiefly tints of brown, and is remarkable for the firmness with which it attaches itself to cotton cloth, particularly when fixed with bichromate of potash, while its modifying effect upon the brighter coal tar dyes is very satisfactory, and its cheapness constitutes an important advantage.

Ingenious attempts have been made by Witt, by Graebe and Liebermann, and others to generalize our knowledge of organic colors, and to determine some definite relation between their composition and tinctorial power, but so far such attempts have had but very limited success.

Mordants.—Among the more recently introduced materials for fixing colors upon cloth may be named silicic acid, obtained by immersion of the cloth in solution of sodium silicate, followed by a dilute acid bath; chromic hydrate from otherwise waste chrome alum; and precipitated sulphur, thrown down by successively passing the cloth through solution of sodium thio-sulphate and hydrochloric acid, useful in fixing aniline green, eosine, etc. In

attaching to cotton the aniline colors, extensive use is made of albumen, "lactarine," and tannic acid, the last named with or without the addition of an antimony salt (tartar emetic). Eosine has been to some extent fixed by means of lead acetate, and calcium phosphate has been employed for some of the aniline dyes.

Dyeing.—The modifications of long established practice in the actual processes of dyeing have been chiefly matters of detail growing out of the extensive introduction of the artificial organic colors, as, for example, the "animalization" of vegetable fibre, and the use of alcohol as a solvent in the dye-vat. It has been proposed to modify the process of dyeing logwood black by using chrome alum (with iron alum and cream of tartar) instead of bichromate before immersion in the logwood bath. The hyposulphites (hydro-sulphites of Schützenberger) have been successfully used for the reduction of indigotine to hydrindigotine in the indigo vat.

Calico-Printing.—The two capital changes in this art have been the introduction, on a great scale, and with remarkable brilliancy and variety of effect, of the coal-tar colors, and the use of pigments, largely of mineral origin, such as chromic oxide, ultramarine, etc., attached to the cloth by the aid of albumen, in the so-called "surface printing." The field of application of both these methods includes the use of sundry colors not available in general dyeing on account of the difficulty of attaching them uniformly over large surfaces of cloth. Among the most important colors to which this remark applies, is the insoluble aniline black of Lightfoot. The exact constitution of this valuable color remains still uncertain, but the conditions for its development upon cloth by the oxidizing action of potassium chlorate, aided by the presence of a minute amount of a copper or vanadium salt, upon a salt of aniline, usually the hydrochlorate, have been carefully examined. It has been reported that cerous sulphate has been for some time successfully substituted for a vanadium compound in this process, the resulting color being found, it is said, even faster than that made with vanadium.

Tanning.—Probably no branch of industry of equal importance with this presents less of notable improvement in its modern history. Such improvement as there has been belongs more to the mechanical than the chemical side of the manufacture. Some few new tanning materials of exotic origin have been introduced, but none upon a large scale, save perhaps Chinese and Japanese galls, which from their price rather fall into dyers' than tanners' hands. The manufacture of tanners' extracts, as of hemlock bark, chestnut oak bark, etc., has been improved, and the use of such materials extended. The substitution of comparatively pure forms of some of the solutions used for the many crude materials formerly employed has made some progress—as, for example, sodium sulphide instead of "rhusma" (orpiment and lime), for liming preparatory to removal of hair and epidermis, and a weak solution of ammonium chloride or hydrochloric acid, instead of dog or fowl excrement for "bating" where lime has previously been applied and the

surplus requires to be removed. None of the many "rapid processes" of ordinary bark tanning can be considered to give altogether satisfactory results; the saving of time is apparently always attended with deterioration of the quality of the leather, particularly as to its durability in use. It has been claimed of late by Böttinger that to *phlobaphene* is essentially due the action of the common oak bark in tanning. In regard to alum tanning, Knapp and v. Wagner have shown some reasons for supposing that the alum and common salt used do not, as is commonly assumed, decompose each other in aqueous solution; but the evidence seems hardly conclusive, and even should the fact be as stated, it might be reversed in presence of the skin in alum tanning. It has been lately proposed to use a salt of iron, ferric sulphate, as a tanning material instead of alum, and still more recently chrome-tanning has been advocated. A method of dyeing, and at the same time partially tanning, raw hide has been introduced in the United States, resulting in the production of a material something like hard vulcanized rubber, and susceptible of a high polish, available for the tips of boots and shoes, and doubtless for various portions of harness and military accoutrements not requiring flexibility. The solutions in which the properly cleansed hide is immersed contain infusion of logwood, nut-galls, cupric sulphate, vinegar, and a salt of iron.

India-rubber, Gutta-percha, etc.—These materials may be briefly noticed here in relation to the manufacture of water-proof clothing, although their applications are so numerous and varied that it is not easy to assign them any single place in a classification of chemical substances founded on their uses. Great extension of the manufactures based upon these substances has for years been going on, but most of the novelty of such manufactures has had reference to varied and chiefly mechanical details of application, not to general chemical treatment. The supply of crude caoutchouc has been greatly increased by systematic search for it in many countries, and from different botanical sources. The quality of the best soft vulcanized rubber has been sensibly improved, as exhibited in the extremely thin and light water-proof garments made from it. A very important improvement has lately been proposed, but the result not yet fully tested by experience, consisting in the admixture with rubber before the vulcanizing process is applied, of ten per cent. or more of very finely subdivided vegetable fibre, the object being to confer a certain degree of porosity so that the objection to rubber clothing, shoes, etc., from the retention of perspiration may be obviated. Perhaps the most noteworthy direction of improvement in the preparation of vulcanized rubber has been that of the production of hard rubber of the higher grades, such as the imitation of ivory for billiard balls, piano keys, etc., by an intimate mixture of caoutchouc and calcined magnesia, strongly compressed and hard vulcanized.

Although of altogether different chemical character, the most

recently introduced and on the whole most important substitute for hard rubber in many of its applications may be mentioned in connection with it, namely, "celluloid," the curious material produced by converting paper into pyroxyline, grinding the product along with camphor so as to secure very intimate mixture, pressing and moderately heating the resultant mass. The extraordinary toughness of this material, giving it a character intermediate between that of vulcanite and horn, the readiness with which its appearance may be modified by coloring matters so as to imitate various natural substances, such as ivory, tortoise-shell, coral, etc., the high polish of which it is susceptible, and its inalterability by water and most other agents likely to be brought in contact with it in common use, have already secured for it extensive employment for a multitude of different purposes.

J. W. MALLET.

(*To be continued.*)

REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

[Continued from p. 212.]

In 1879 E. Salkowski* made the observation that human urine distilled with tartaric acid yielded in the distillate a body which was characterized by a red color when treated with pure nitric acid. Later he has shown that the body does not exist free in urine, but is a product of the action of tartaric acid. Munk has found the same substance in the contents of the small intestines, and Salkowski has found that it is formed from albumin by pancreatic fermentation even in 14 hours, and by the continued digestion of horn substance he has succeeded in isolating considerable of the body, together with indol and phenol. The body thus formed is an acid of slight aromatic odor, and after repeated crystallization from alcohol has much the appearance of benzoic acid; analysis shows it to be phenylacetic acid. Further investigation by E. and H. Salkowski† has shown that by the pancreatic digestion of albumin another aromatic acid is formed. Flesh thoroughly extracted with water and alcohol and then dried was the material used. 125 grams of this tissue with 3 litres of water, 9 grams of sodium carbonate, and the pancreatic gland of a dog, were digested 13 days at 40° C. After the removal of the albumin by boiling, and the higher fatty acids by separation as baryta soaps, fractional distillation was resorted to, whereby butyric and valeric acids were removed. The fraction obtained above 250° C. solidified on cooling to a crystalline mass, which, after purification, furnished .7 gram of white crystals. The acid thus obtained was phenylpropionic or hydrocinnamic. From warm concentrated aqueous solutions it separates as an oil, from dilute solutions as glistening needles melting at 47–48° C., and giving by oxidation benzoic acid.

* Zeitschr. für physiolog. Chemie, 2, 420. † Ber. d. d. chem. Gesell. 12, 107.

Phenylpropionic acid was also found in fresh flesh. The relation of phenylacetic acid to indol is a very suggestive one. The formation of indol by the pancreatic digestion of albumin was first suggested by Kühne, but lately both Kühne and Nencki have explained clearly that indol is simply a product of the putrefaction of albumin and not formed by the pancreatic ferment, and it is quite probable that the phenylacetic acid also is simply the product of the putrefaction of albumin, but this does not hinder its formation in the body, for that putrefactive changes take place in the intestinal canal is a well established fact.

Recently Baeyer* has effected the synthesis of oxindol, and he considers it to be simply the inner anhydride of orthoamidophenylacetic acid, this latter body being formed from phenylacetic acid by a simple process. The oxindol formed from phenylacetic acid by Baeyer's process gives, when heated with zinc dust, indol, and in all other respects shows itself to be pure oxindol. So that it appears quite plausible that phenylacetic acid and indol, as regards their formation by pancreatic fermentation, stand in close relationship to each other, which could perhaps be explained by a comparison of the quantitative proportions of each substance at different stages of the putrefaction. It has also been pointed out that phenylpropionic acid may stand in similar relations to skatol.

In order to ascertain if different kinds of albumin would yield these two aromatic acids, E. and H. Salkowski† conducted a number of experiments, both with and without the addition of any pancreatic fluid. Their method was to digest 50 grams of the dry albumin with 1 litre of water containing 15 cc. of a saturated solution of sodium carbonate at 40° C., occasionally adding a few drops of a solution containing *Bacillus subtilis*. After a longer or shorter time (2½–60 days) the mixture was distilled to about one-sixth of its volume and both residue and distillate examined. In this way blood-fibrin and muscle-fibrin yielded constantly from 2½–13 days phenylpropionic acid to an amount never exceeding .5 per cent. of the dry albumin. Serum-albumin after 37 days digestion furnished phenylacetic acid in considerable quantity; traces of the acid were to be found even after 13 days. In the fermentation of flesh succinic acid was found in not inconsiderable quantity at the first stage of the decomposition, being detected even after 20 hours. It was also noticed that both horn substance and serum-albumin differ from flesh in that they do not so readily undergo the fermentation. In all experiments with flesh the ether extract contained considerable quantities of the higher fatty acids, principally palmitic acid, and when the fermentation had not been of too long duration, oleic acid also, the acids being found to the extent of 3 per cent. of the dried albumin. In these cases the flesh was previously freed from fat by repeated heating with ether. Serum-albumin likewise yielded fatty acids, and these two facts have a significant bearing on the

* Ber. d. deutsch. chem. Gesell. 12, 582. † Ibid. 12, 648.

possibility of the formation of fat from albumin by processes taking place normally in the animal body. The principal part of the distillate was composed of indol, skatol and phenol.

Hippuric acid is well known as a characteristic constituent of the urine of herbivorous animals. It is also well known as a constituent, in far smaller quantity, however, of human urine and the urine of carnivorous animals, being found in the latter case even when the animal is completely deprived of vegetable food.

Now since E. and H. Salkowski have found that albuminous substances constantly furnish aromatic acids by pancreatic fermentation, or, in other words, that flesh and fibrin furnish regularly phenylpropionic or hydrocinnamic acid, they have proposed the theory that these aromatic acids formed by the breaking up of albumin in the body become oxidized to benzoic acid, and that in this manner hippuric acid might originate from albuminous substances. They have thus been led to study the behavior of phenylacetic and phenylpropionic acid in the organism *

A support for such a theory was found in the discovery by Erdman and Marchand† in 1842 that cinnamic acid changed within the organism to hippuric acid, which statement was confirmed by Graebe and Schultzen.‡

E. and H. Salkowski find by experiment that their supposition is partially correct. Phenylpropionic acid is changed within the body completely into benzoic acid, and appears as hippuric acid in the urine. Phenylacetic acid, on the other hand, is not oxidized, but forms an acid analogous to hippuric acid, which is properly called phenaceturic acid.

Phenylpropionic acid, $C_6H_4CH_2CH_2COOH$, was given to a dog in food (1.5–2 grams of a soda salt daily) and the urine collected and evaporated. In the alcoholic ether extract hippuric acid alone was found, which, heated with hydrochloric acid, decomposed with formation of benzoic acid; no trace of an homologous acid was found. Thus we have a lucid explanation of the hitherto inexplicable phenomenon of the secretion of hippuric acid by animals fed entirely on flesh; for as the phenylpropionic acid is formed very early by pancreatic fermentation, it is clearly not difficult to accept the view that during life a certain quantity of this acid is formed in the intestinal canal. The hippuric acid of herbivorous animals without doubt originates also in part from albumin in this manner. The fact that a hungry animal which lives simply on its own tissue continues to secrete hippuric acid is another indication, as is also the secretion of indican during the condition of hunger, that in tissue and organs also fermentation processes take place which lead to the splitting off from albumin of aromatic substances.

Phenylacetic acid, $C_6H_5CH_2COOH$, was fed in the same quantities as the phenylpropionic acid to several dogs, and phenaceturic acid was found abundantly in the urine, but hippuric acid never rose

* Ber. d. deutsch. chem. Gesell. 12, 653. † Jour. für prakt. Chem. 26, 494.
‡ Annal. Chem. u. Pharm. 142, 346.

above the normal amount. The phenaceturic acid thus formed does not differ in many of its properties from hippuric acid, crystallizing from hot water in thin plates, and when boiled with hydrochloric acid breaking up easily into phenylacetic acid and glycocoll. Its formula is therefore—

$$\begin{array}{l} CO—CH_2—C_6H_5 \\ | \\ NH—CH_2—COOH, \end{array}$$

while hippuric acid is

$$\begin{array}{l} CH_2—COOH \\ | \\ NH—CO\,.\,C_6H_5. \end{array}$$

Several years ago Baumann, while studying the origin of aromatic substances in the body, made experiments which tended to show that under certain conditions phenol is formed during the putrefaction of albumin. The natural supposition was that the phenol is not a direct decomposition-product of albumin, but more probably of the tyrosine formed from albumin. More recently Baumann, in conjunction with Brieger,* has shown that the phenol formed from albumin by putrefactive changes consists in great part of paracresol, and contains only a small proportion of phenol, C_6H_6O. Weyl† has, however, shown that by putrefaction tyrosine can be decomposed with formation of volatile phenol, and at the same time paracresol is formed. Again, Baumann,‡ by experiments on dogs, has shown that the paracresol which appears to a great extent as paracresol-sulphuric acid in the urine, is to a small extent oxidized in the body to paroxybenzoic acid, while the paroxybenzoic acid is decomposed, partially in the body, completely by putrefaction, into phenol and carbonic acid.

In a more recent contribution Baumann§ has attempted to show the relation of these different aromatic bodies as regards their formation, starting with the assumption that they are formed not directly from albumin but from tyrosine. He subjected 6 grams of tyrosine in 5 litres of water to decomposition at 40° C. with a small quantity of pancreas infusion for 2 days. At the end of this time the evaporated fluid yielded no trace of tyrosine crystals, but by proper treatment an acid was obtained which, by recrystallization, showed itself in well formed crystals, and had the properties and composition of hydroparacumaric acid. Thus Baumann arrives at the conclusion that this acid is the first decomposition-product of tyrosine by putrefaction, and that it originates from tyrosine in the same manner as succinic acid from aspartic acid. This decomposition is also of interest as showing something in regard to the constitution of tyrosine. Barth‖ had previously shown that tyrosine belongs to the paroxybenzoic acid series, and from his experi-

* Zeitschrift für physiolog. Chem. 3, 149. †Ber. d. deutsch. chem. Gesell. 12, 354.
‡ Zeitschrift für physiolog. Chem. 1, 244. § Ber. d. deutsch. chem. Gesell. 12, 1450.
‖ Ann. Chem. u. Pharm. 136, 110, also 152, 96.

ment concluded that tyrosine is paroxyphenolamidopropionic acid (amidohydroparacumaric acid).

Thus according to Barth the constitution of tyrosine would be expressed by the following formula:

$$C_6H_4\begin{cases}OH\\C_2H_3\,.\,NH_2COOH,\end{cases}$$

and this view receives an additional support in the formation of hydroparacumaric acid from tyrosine. The series of phenol-derivatives formed from albumin, or more properly from tyrosine, has been increased by the observations of E. and H. Salkowski,* that by the putrefaction of horn substance and of albuminous matters in general, oxy-aromatic acids are obtained, viz., paroxyphenylacetic acid and paroxyphenylpropionic acid. Thus, according to Baumann, the following series of compounds can be formed from tyrosine by gradual decomposition and oxidation:

$$\underbrace{C_9H_{11}NO_3}_{\text{Tyrosine}}+H_2 = \underbrace{C_9H_{10}O_3}_{\text{Hydroparacumaric acid}}+NH_3$$

$$\underbrace{C_9H_{10}O_3}_{\text{Hydroparacumaric acid}} = \underbrace{C_8H_{10}O}_{\text{Paraethylphenol}}+CO_2$$

$$\underbrace{C_8H_{10}O}_{\text{Paraethylphenol}}+O_3 = \underbrace{C_8H_8O_3}_{\text{Paroxyphenylacetic acid}}+H_2O$$

$$\underbrace{C_8H_8O_3}_{\text{Paroxyphenylacetic acid}} = \underbrace{C_7H_8O}_{\text{Paracresol}}+CO_2$$

$$\underbrace{C_7H_8O}_{\text{Paracresol}}+O_3 = \underbrace{C_7H_6O_3}_{\text{Paroxybenzoic acid}}+H_2O$$

$$\underbrace{C_7H_6O_3}_{\text{Paroxybenzoic acid}} = \underbrace{C_6H_6O}_{\text{Phenol}}+CO_2$$

With the exception of paraethylphenol and paroxybenzoic acid, all of these substances have been detected in the animal body, or by the decomposition of albumin or tyrosine. Paroxybenzoic acid originates in the animal body from paracresol, and it is not found in the urine under normal conditions, according to Baumann's view, simply because the quantity of paracresol is very small. Baumann† is of the opinion that the tyrosine formed in the intestinal canal, as an intermediate product in the decomposition of albumin and readily passing into hydroparacumaric acid, splits up in the body and furnishes the paroxyphenylacetic acid which is

* Ber. d. deutsch. chem. Gesell. 12, 1438; 13, 189. † Ibid. 13, 279.

found in the urine, an acid very similar to hydroparacumaric acid. The quantity of this oxy-acid detected in human urine was quite similar in ten different experiments, 25 litres of urine furnishing in each case about ½ gram of the crude acid.

As Weyl* has shown that by putrefaction paracresol is formed both from paroxyphenylacetic acid and tyrosine, it is quite clear that tyrosine must be the mother substance from which the paroxyphenylacetic acid found in the urine originates.

Baumann then observes that if the different bodies placed in the above list are formed successively from one another by putrefaction, paraethylphenol or paroxyphenylacetic acid must be formed from hydroparacumaric acid. In order to ascertain this point the following interesting experiment was conducted on a man, and as preliminary to the actual experiment the following facts were ascertained: The normal daily urine (1260 cc., sp. g. 1.026) did not contain a sufficient amount of the aromatic oxy-acids to permit of their separation in pure condition; further, this quantity of normal urine contained 2.636 grams of sulphuric acid in the form of sulphates, and 0.372 gram of sulphuric acid existing in the form of ethylsulphuric acid. 100 cc. of such normal urine furnished by distillation with hydrochloric acid a distillate which was simply made turbid by bromine water, phenol not being found in weighable quantity. On the following day 5 grams of pure hydroparacumaric acid were dissolved in water and taken at intervals during one hour. The urine of the following 24 hours (1325 cc., sp. g. 1.027) contained 2.207 grams of sulphuric acid in the form of sulphates, and 0.479 gram of sulphuric acid existing as ethylsulphuric acid. 100 cc. of the same urine furnished by distillation with hydrochloric acid a fluid which, with bromine water, quickly gave a crystalline precipitate of a bromine compound of phenol weighing 0.031 gram. From the entire quantity of the urine 0.8 gram of an acid was obtained which, after recrystallization from benzol, was found to be pure hydroparacumaric acid. Thus the greater part of the hydroparacumaric acid given had disappeared in the body, while one part was secreted unaltered, and a still smaller part was decomposed with formation of phenol, which was secreted by the urine as ethylsulphuric acid. Paroxyphenylacetic acid was not formed from the hydroparacumaric acid in a quantity sufficient to be detected.

Baumann then, in discussing the possibility of these different aromatic bodies being formed from each other by alternate oxidation and reduction, suggests that hydroparacumaric acid, under certain conditions, may furnish paroxyphenylacetic acid directly by splitting off of carbonic acid and ammonia, and in support of such a decomposition quotes the behavior of leucine by putrefaction in the presence of air, by which ammonia, carbonic acid and valeric acid are formed.

* Ber. d. deutsch. chem. Gesell. 12, 354.

R. H. CHITTENDEN.

(*To be continued.*)

THE SUBSECTION OF CHEMISTRY AT BOSTON.

At the Boston meeting of the American Association for the Advancement of Science, the subsection of chemistry was more largely attended then ever before. The prospects are that in another year it will be raised to the dignity of a full section, to be presided over by one of the Vice-Presidents of the Association. At the late meeting Professor J. M. Ordway occupied the chair, and Professor C. E. Munroe was secretary. Next year, in Cincinnati, Professor W. R. Nichols will be chairman, and Professor H. W. Wiley secretary. Prof. G. J. Brush was elected President of the Association.

The Association came together on Wednesday, the 25th of August. On Wednesday and Thursday little real work was done, the first day being devoted to organization and to set addresses, and the second to a visit to Cambridge. Professor Ordway's address as chairman of the subsection was delivered on Wednesday afternoon. It consisted mainly of a brief resumé of late advances in chemistry, especially in some of its applications to the useful arts, and of a plea for the more extended study of the biological side of the science.

On Friday the reading of papers before the subsection began. The first communication was by Professor Wiley, who spoke upon "The rotatory power of glucose and grape sugar." The word "glucose" is applied by the manufacturers to the thick syrup made from corn. The term "grape sugar," on the other hand, is applied to the crystallized product. There are now ten glucose factories running night and day in this country, which consume twenty-one thousand bushels of corn per diem, each bushel yielding on an average twenty-eight pounds of glucose. The yearly yield is therefore 214,620,000 pounds. Five-sixths of this product is "glucose," and one-sixth "grape sugar." The latter is used for mixing with cane sugar by brewers, distillers, vinegar makers, etc. The mixture with cane sugar is sold as "new process sugar." The "glucose" is used also by brewers and distillers, for sizing paper, in making printer's ink rollers, and in enormous quantities for syrup. It is mixed with a few per cent. of cane syrup and sold under a variety of fancy names. Professor Wiley has found that all the commercial glucoses contain notable percentages of dextrine, and upon the latter their rotatory power largely depends. Formulae were given for determining the per cent. of glucose by the polariscope.

Next came one of Professor Leeds' papers on the "Influence of actinism upon iodides."* It was read by D. S. Martin, the author being absent. E. T. Cox followed with an account of some extensive lodes of oxide of antimony in Sonora, Mexico This paper was partly geological in character. The lodes described are from four to twenty feet wide, and exploration to the depth of thirty

* Published in full by the American Chemical Society.

feet shows that the fissures are filled from wall to wall with the hydrated oxide, almost pure. The ore contains from 60 to 77 per cent. of metal, and the entire deposit probably averages 50 per cent. By going down deeper the oxide may perhaps change to sulphide; but at present there is no evidence of any such alteration. The slight impurity in the ore is silica.

The fourth and fifth papers were by Professor E. W. Morley, who described some tables for use in gas analysis, and recommended a thermometric scale which shows the logarithmic factor for reduction to zero. This is convenient when many analyses are to be made.

The next paper, on "The constitution of the tartrates of antimony," was the joint work of F. W. Clarke and Miss Helena Stallo. It will appear in full in this journal, and needs therefore no detailed notice here. It was followed by a communication from Thomas Gaffield, entitled "The action of sunlight on glass." A general classification of the changes of color produced by the sun in nearly colorless glasses, is as follows: 1. From white to yellowish. 2. From greenish to yellowish-green. 3. From brownish-yellow and greenish tints to purple. 4. From light green or greenish white to bluish. 5. From bluish and other tints to darker shades of the same colors. Every specimen of colorless glass exposed for ten years shows some change of color, with the exception of some white flint glass, such as is used for fine glassware and optical purposes. The optical glasses studied by Mr. Gaffield, except two pieces of crown glass which became of a yellowish color, showed only very slight changes of tint. Possibly the oxide of lead, which enters largely into the composition of such glass, may act as a protector against changes by sunlight exposure. In experimenting for ten years with colored glasses of the main spectral colors, no change was observed in any pot-metal specimens, save a slight darkening of the purple. A change to a purplish or yellowish color was noticed in the colorless body of some of the flashed and stained specimens, which were originally tinted on the surface only. An experiment with pot-metals, not of the primary colors, but of the hues which most nearly approach those produced in colorless glass by sunlight exposure, showed the following changes: 1. From brownish tints to a flesh-color. 2. From flesh-color to violet or purple. 3. From amber, olive, and purple to darker shades of the same colors. It is interesting to know that, so far as such colors were used in the old cathedral windows, they must have changed in tint; and that the glass which we now see in these old churches and which has suffered sunlight exposure for centuries, is of very different hues from those which it exhibited when it left the artists' studios or the glass factories of mediæval times. A curious fact noticed by Pelouze and by Percy is confirmed by Mr. Gaffield; namely, that with a few exceptions among the colored glasses, all the specimens changed in color by sunlight can be restored to their original tint by the heat

of a glass-stainer's kiln. They can again be colored by exposure to sunlight, and this coloration and the decoloration by heat can be carried on indefinitely.

The day's work concluded with two papers by Professor Morley, concerning the ratio of oxygen to nitrogen in air. He presented the following remarkable conclusions. When the air at a given place is cold and the barometer high, there may be a vertical descent of cold air from great altitudes. Samples collected at such times are more likely to approach the composition of the upper atmosphere than those collected at other times. If there be any cause tending to produce an excess of nitrogen in the upper atmosphere, such as, for example, the difference in density between oxygen and nitrogen, then the average per cent. of oxygen in many samples collected at the times above mentioned will be lower than that of other samples. In order to test this supposition, Professor Morley collected samples of air during each time of unusual cold and high barometer from September, 1878, to April, 1879. In 1878 the mean percentage of oxygen in these was 0.16 per cent. lower than in other samples; and in 1879, 0.12 per cent. lower. No source of error could be detected. The inquiry was further pursued by a series of daily duplicate analyses of air during six months, and a comparison of the results with the thrice daily maps of the U. S. Signal Service. He finds a deficiency of oxygen at the times and only at the times when a vertical descent of air at or near the place of collection may reasonably be inferred from the weather maps. The coincidences were plotted by Professor Morley in a series of curves, and are certainly extraordinary.

On Saturday Mr. N. B. Webster spoke "On a solution of ferric gallate and ferric oxalate as a reagent for the quantitative analysis of ammonia." Then C. F. Mabery described some substituted acrylic acids recently investigated by himself with the co-operation of Mrs. R. Lloyd. Diodbromacrylic acid, $C_3I_2BrHO_2$, is made by the action of iodine upon brompropiolic acid. It crystallizes in flat, white, six-sided plates, which are sparingly soluble in cold, readily in hot water; soluble also in ether, benzol, carbon disulphide and ligroin. It readily decomposes carbonates. Melting-point, 160°. Its silver, potassium, calcium and barium salts were prepared and analyzed.

Fuming hydrochloric acid unites readily with brompropiolic acid to form chlorobromacrylic acid, $C_3ClBrH_2O_2$. It forms elongated flat prisms which melt at 70°. In solubility it resembles the acid previously described. Its acid character is very decided, and its silver, potassium, calcium and barium salts were investigated.

Next in order Mr. L. M. Norton discussed the valuation of indigo; after which Professor W. O. Atwater spoke on "The soil supply of nitrogen for plants." The gist of his paper was briefly as follows: Nitrogen is rapidly wasted from the soil, and is the most expensive material to replace in the form of manures. In this country, especially in New England, we have longer and colder

winters, with warmer and drier summers, than in Europe. Less of our rain and snow water escapes from the soil in winter with us than abroad, since our ground is frozen longer; while in summer the same is true because of greater evaporation from the surface. Hence in our climate less nitrogen is lost by the soil through leaching than is lost in Europe. Professor Atwater's experiments, carried out in the field by himself and by colleges and private individuals in several States, establish the foregoing conclusions, and show that nitrogen is not so necessary in our soils, and that we can get along with the cheaper mineral fertilizers and less nitrogen than our European competitors.

The next communication was by Professor H. B. Nason, who described some "Incrustations formed in pipes used in gas wells," and exhibited an interesting specimen. Professor W. R. Nichols gave an account of some "Observations on the temperature and chemical character of Mystic Lake, Mass., at different times and at different depths," and Professor C. E. Munroe proposed a "Modification of Berthier's process for the valuation of coal." He substitutes for the crucible used by Berthier an iron tube three feet long and one inch in diameter, open at one end and having a screw plug at the other. The litharge and coal are placed in this tube, which is then heated in a furnace under a steam boiler for about five minutes. The tube, while red-hot, is held vertically in a vise, the plug is withdrawn, and the molten lead is collected in a box lined with plaster of Paris. This process is especially devised for the use of steamship engineers when making purchases of coal.

On Monday but few papers were read before the sub-section. J. L. Kleinschmidt spoke of "Foreign substances in iron"; S. P. Sharples discussed the "Commercial testing of sugar, illustrated by samples of sugar and the instruments used"; and Professor Wiley described the "Influence of heating with dilute acids, and shaking with bone coal, on the rotatory power of glucose." He finds that heating with acids produces a marked effect, diminishing the rotatory power of glucose by one-half. When this fact is not taken into account, a serious error may arise in the estimation of a mixture. The stronger the acid and the longer the heating is continued, the more marked is the effect. Simultaneously with this diminution of rotatory power, the percentage of glucose or of copper-reducing matter may be greatly increased. This shows that intermixed dextrin or other optically active substance is either changed into glucose or has its rotatory power altered. By shaking glucose with animal charcoal, a decided change is effected in its rotatory power, sometimes as much as ten per cent. Thus, in the examination of mixtures, serious errors may arise if bone coal has been used, unless the effect of the latter is taken into consideration.

The closing paper of the day was by Dr. T. Sterry Hunt, "On the genesis of certain iron ores." It is impossible to state Dr. Hunt's conclusions compactly enough for present purposes, and at the same time accurately. He begins with the iron, generally fer-

rous iron, found in the mineral silicates of crystalline rocks. This, by sub-aerial decay, is liberated as ferric hydrate, which in turn is reduced to ferrous hydrate by organic matter, and dissolved in water either charged with carbonic acid or acids of organic origin. From such solutions it is again deposited as limonite, as siderite, as a silicate, or as pyrites, in all of which conditions iron is found in sedimentary formations. The intervention of soluble sulphates, and their reduction through organic agency to sulphides, determines the formation of pyrites in sediment. The changes of siderite and pyrite under atmospheric influences were considered. The latter, by oxidation, yields sulphate, which by the intervention of water holding carbonates, conjointly with oxygen, is converted into hydrous peroxide. Evidence, both experimental and geological, was cited by Dr. Hunt in support of his conclusions.

On Tuesday, E. G. Love presented a communication on "The illuminating gas of New York city," after which two papers were read by A. A. Breneman. The first of these, upon "New colors for salt-glazed pottery," was accompanied by the exhibition of specimens. A vase was shown upon which a vine in green was painted on the ordinary gray body of the stoneware. The range of obtainable colors is very great, so that this cheap ware may be made the basis of a new process of under-glaze decoration in which the entire piece, color-glaze and body, may be completed in a single burning. Professor Breneman's second paper was entitled "Notes on water analysis." It related to the significance of chlorine in sanitary analyses of water; to the destruction of organic matter by aeration in running streams; to the volume of liquid most suitable for the ammonia titration, the author preferring 100 cc.; and to improvements in the Nessler test.

Next came two papers by Professor Atwater, one on the determination of sulphuric acid, the other on the quantitative estimation of fats; and a communication by E. L. Nichols on "Salt solutions and the absorption of gases." Professor Munroe followed with a paper upon "The action of vegetable acids on tin," in which he showed that the metal in question is acted upon and dissolved by such acids as are found in fruits. Cider which had been kept for a short time in a tin fountain contained 117 milligrammes of tin to the litre. Fruits canned in tin become contaminated with it, and have produced poisoning. He found also that tin reduces lead from its solutions in these acids, excepting acetic acid, and he suggested that our tin culinary utensils had probably protected us to some extent from lead poisoning. Specimens of block tin pipe were shown which had been acted upon by well water, an action which Professor Munroe attributed to humic and ulmic acids.

Papers were also presented by William McMurtrie "On the deficiencies of meteorological work in data of value to agriculture, and the means for supplying them"; by W. Colegrove, on "The direct combination of hydrogen and nitrogen"; by G. F. Kunz, on "The density of a large diamond"; and by L. P. Kinnicutt on

"The substitution of cones made from parchment paper for platinum cones in Bunsen's process of filtration."

Wednesday, September 1st, was the closing day of the meeting. Before the chemists four papers were read by Professor Atwater, and one by C. F. Mabery, on "The crystallographic determination of the form of mucobromic ethyl ether." Professor Atwater's papers were as follows: "The chemical composition and nutritive values of fish"; "The determination of nitrogen by the hypobromite process"; "Some new forms of apparatus," and "The determination of phosphoric acid by the molybdic process." The paper upon fish gave the results of an investigation made for the United States Fish Commission, and included analyses of a large number of specimens of the more common edible species. Some of the percentages of edible solids in various kinds of fish are as follows. The whole fish as sold in the market, waste and all, is put at 100.

Flounders	7.1	Shad	14.8
Cod	10.5	"	18.7
Mackerel	11.4	Lake trout	13.6
Halibut, lean	15.6	Salmon	25.6
" fatter	27.2		

There is no evidence to show that the flesh of fish is richer in phosphorus than other meats are, nor that, if it were so, it would be on that account more valuable for brain food.

In closing this report, reference may properly be made to an account read before the geologists of the Association by Professor C. H. Hitchcock, on the occurrence of tin ore at Winslow, Maine. The locality was described, specimens of cassiterite from it were exhibited, and a bar of tin made from the ore, weighing fourteen ounces, was shown. Professor Hitchcock considers the locality the most promising for tin yet discovered in this country.

F. W. CLARKE.

NOTES.

Ozone in the Air.

For many years the question concerning the occurrence of ozone in the air has been regarded as satisfactorily answered, and little doubt has been expressed regarding its presence. The influence

exerted by ozone upon those who breathe it has been discussed very fully; efforts have been made to secure regular systematic observations on the amount of ozone present in the air, and it is safe to say that millions of such observations have been made and many of them recorded. It is hence somewhat startling to find that one of the most careful chemical investigators, one who has acquired an enviable reputation by his painstaking investigations on hydrogen peroxide, E. SCHÖNE, should at this late day seriously question the proofs which have hitherto been adduced for the purpose of demonstrating the presence of ozone in the air. Indeed he feels warranted in stating that "*as yet we possess no chemical reaction by means of which we can prove the existence of ozone in the air.*" The proofs which have been brought forward are mainly those of Schönbein.

Schönbein bases his belief upon three reactions: 1. Something in the air sets iodine free from potassium iodide and caustic potassa is formed. 2. Papers saturated with a solution of manganese sulphate are turned brown in consequence of the formation of Mn_2O_3. 3. Thallium suboxide is oxidized to thallium oxide. But Schöne's investigations have shown that these changes of potassium iodide and thallium suboxide can be effected as readily by hydrogen peroxide as by ozone, and hence the reactions by no means prove the presence of ozone in the air. So also the change of manganese sulphate does not require the presence of ozone, as it is effected by air free from ozone, in which a trace of ammonium carbonate is present; and as this latter substance is normally present in the air, the proof based upon the change of the manganese sulphate papers loses its value. The proofs brought forward by Houzeau and later by Andrews are based indirectly upon the supposed absence of hydrogen peroxide, but since this substance has been shown to be present in the air the proofs are worthless.

The only known reagent by means of which the existence of atmospheric ozone could be positively proved is metallic silver. But no one of the observers mentioned above has ever noticed a blackening of silver in normal air free from sulphur compounds, and Schöne himself has been unable to detect more than the slightest change in color of silver foil exposed for long periods to the action of the air.

As regards the supposed formation of ozone during thunder storms, the odor of the air noticeable under these circumstances is not, as Schöne states, that of ozone, and further it is difficult to see how ozone could be formed by lightning, as the electric *spark* in a mixture of oxygen and nitrogen causes the formation of only hyponitric acid, while the silent discharge is necessary for the formation of ozone. Schöne does not deny that ozone may be present in the air, but simply shows that at present we possess no valid proof of its presence. (*Ber. d. deutsch. chem. Gesell.* 13, 1503.)